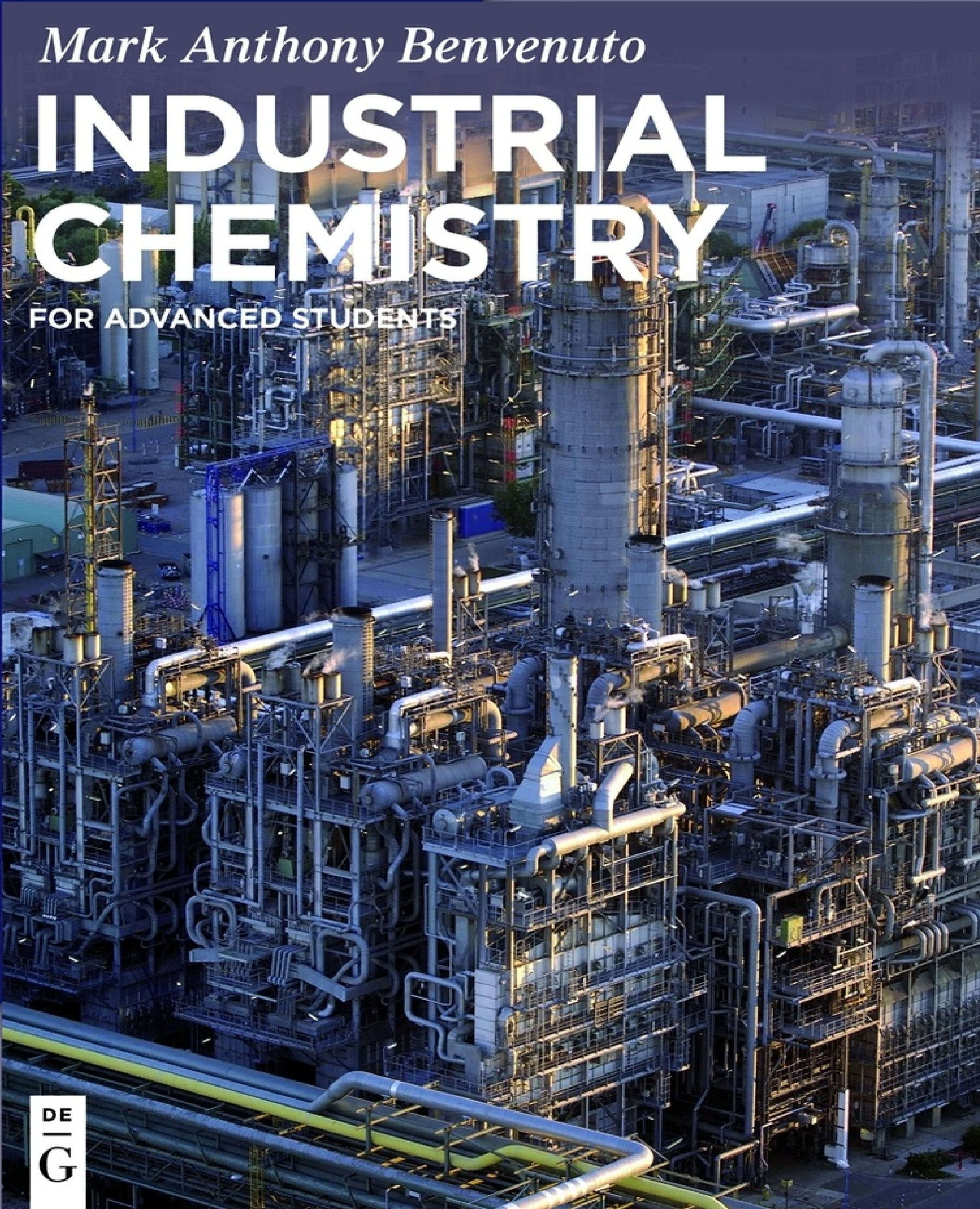
DE GRUYTER

GRADUATE

Mark Anthony Benvenuto

INDUSTRIAL CHEMISTRY

FOR ADVANCED STUDENTS



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Industrial Chemistry

For Advanced Students

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Preface

The production of tens of thousands of commodity chemicals today yields a quality of life for many people which has never before been experienced throughout the rise and fall of all civilizations. Because of the ability to refine and use numerous chemicals from crude oil, we have a wide variety of long-lasting, durable plastics that help enable everything from modern medicine to long-distance food transport. This same source provides us with huge quantities of several different motor fuels which enable transportation that is far faster than anything that had been possible throughout most of history. Because of our ability to refine, isolate, and alloy more than 60 elemental metals, we have been able to do everything from creating new building materials to mass produce tiny magnets that enable cellular phones and a myriad of other electronic devices. Because of our ability to refine and use chemical commodities such as cement, concrete, and asphalt, we have been able to construct an infrastructure for humanity that again has never been accomplished, even in the most advanced cultures of the past.

Many of the largest produced commodity chemicals worldwide have been discussed in detail in the volume *Industrial Chemistry*. We will see in this book that many of the substances discussed in the first volume are used in chemical transformations that either produce or utilize the chemicals discussed here. But in writing a single volume, one has to make several painful choices about what is included, and what must be excluded, from the contents. *Industrial Chemistry – for Advanced Students* is not only picking up where *Industrial Chemistry* left off however; it is also widening the discussion and examination of the industrial-scale chemical processes and end products that make vital contributions to our world today.

This volume’s goal is to help students see the interconnectivity of a widely differing series of chemical processes and to relate what they have learned in other chemistry classes to the world of industrial-scale chemistry.

Writing a book like this is both a challenge and a reward, and there is probably no author alive who can do it without help. I have to thank my editors, Karin Sora and Julia Lauterbach for help and advice at every step of this book’s development. Many of my work colleagues have been very helpful when it came to everything from chasing down the details of some process to double checking how ideas are presented in the chapters. Thanks are definitely due to Drs. Klaus Friedrich, Matt Mio, Liz Roberts-Kirchhoff, Shula Schlick, Mary Lou Caspers, Kate Lanigan, Kendra Evans, and Jon Stevens, and also to Jane Schley and Meghann Murray. Additionally, I thank Heinz Plaumann, Hulya Ahmed, and Denise Grimsley of BASF, Keith Olsen and Kevin Perry of General Motors, and Felix Schneider, formerly of the US Food and Drug Administration, for tolerating what may have seemed like an endless stream of apparently random questions from me. A very special thanks goes to Megan Klein of Ash Stevens for proof reading the entire manuscript. And obviously, many thanks go to my wife, Marye, and my sons, David and Christian, for just plain putting up with me as I wrote this book.

Detroit, January 2015

Mark A. Benvenuto

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1 Overview and introduction to the chemical industry

1.1 Focus and depth

Over 70,000 chemicals are produced annually on a large scale and are either used in some further chemical transformation, or are incorporated into an end product. Perhaps obviously, nothing short of an exhaustive encyclopedia could discuss all of them, or even list all their uses. Some focus is required in order to cover a selected series of topics within this extensive, broad field.

Similarly, it would be difficult to produce a volume that simply lists a series of chapters corresponding to the largest commodity chemicals used in the world today which were left out of *Industrial Chemistry*, because such a “laundry list” does little to place any of these chemicals and materials in a larger context. This book will attempt to discuss the large process chemistry omitted in the initial volume and will also build greater context among the processes. Thus, while there are chapters on chemicals that are certainly organic – those that are only produced from the refining of crude oil –as well as on those that are distinctly inorganic, there are also several chapters that straddle borders, such as hydrogen peroxide, food additives, bromine, fluorine, and asphalt.

Most developed nations track self-determined lists of materials that are deemed vital to their economies and defense. For example, in the United States, the Department of Energy maintains a *Critical Materials Strategy* (Department of Energy , 2014), the Department of Defense has published a *Strategic and Critical Materials 2013 Report on Stockpile Requirements* (Department of Defense, 2014), and the United States Geological Survey produces a *Mineral Commodities Summary* each year (United States Geological Survey, 2014). These reports indicate the quantities of various chemicals that are produced annually and how much the United States imports from other nations. Similar documents are produced by the ministries of defense, education, and economic growth in most European and Pacific nations. In addition to these, several national and internationally learned societies keep track of chemical and material production, and usually publish their own lists and compilations of statistics regarding them (Chemical and Engineering News, 2014; Royal Society of Chemistry, 2014; European Chemical Industry Council, 2014; Society of Chemical Manufacturers and Affiliates, 2014; Gesellschaft Deutscher Chemiker, 2014; Chemical Society of Japan, 2014; Royal Australian Chemical Institute, 2014; International Union of Pure and Applied Chemistry, 2014). Also, trans-national organizations like the United Nations and the Arctic Economic Council monitor chemical production and industrial use in their annual reports and in more targeted documents (United Nations Environment Programme, 2012; United Nations Environmental Programme, 2014; Arctic Council, 2014).

The chemicals and materials in these chapters are not always produced on a large enough scale that they make it on to any “top 100” list of the above-mentioned organizations. But each material is vitally important in some way, and thus is worthy of discussion. Therefore, we have tried to include many of them in this book.

1.2 Recycling

There is no doubt that the chemical industry today has been greatly transformed from the industry of the 1960s. It has been noted that from 1945 to perhaps 1965, the generation that had fought the single largest war humanity had ever seen returned home and built a society and a quality of life that had also never been seen before. The infrastructure in the countries that had been embroiled in that war expanded greatly, which meant the use of millions of tons of refined metals, concrete, asphalt, glass, and petroleum products – the latter was in part for the fuels for the vehicles that made this all happen. Highways were constructed, cities built or rebuilt and water and energy infrastructures were put in place or replaced. All of this required massive amounts of chemicals and all of it generated waste.

The developed world has changed since that time. Now there is recognition that this level of man-made change has affected the world itself. While debate continues over resource depletion, climate change, the first priority use of arable land and the pollution of fresh and salt waters, the chemical industry has adapted and has moved toward cleaner, more environmentally benign practices for many of the production streams that manufacture and refine the chemicals we use today.

A part of each chapter in this book has been devoted to the concept of recycling and reuse of the material upon which it focuses. When no recycling or reuse is possible, this is acknowledged. But when some process has been improved, made safer, or made economically more sound through the practices of good stewardship on the part of producers, including recycling or reuse, that too is also acknowledged.

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2 Phosgene (carbonyl dichloride)

Throughout history, certain chemicals or materials have gained fame or notoriety for a wide variety of reasons. Gold has been valued in almost all civilizations from ancient times to the present for no reason except its visual beauty. Iron has been valued because of its ability to hold an edge, which makes it useful in forming tools and weapons. Arsenic and arsenic compounds have been known to be poisons in several cultures – and indeed, have been considered a weapon within an assassin’s arsenal for hundreds of years. More recently, both phosgene and one of its starting materials, chlorine, have been considered one of the worst of battlefield weapons, namely, poison gas.

Elemental chlorine gas was indeed the first chemical warfare agent widely used on the western front of the First World War. Although the gas is poisonous, at the concentrations that were delivered by artillery in that war, it was seldom lethal by itself. It is denser than air, thus seeping and pouring into the trenches, forcing soldiers without gas helmets to rise up for air, where enemy soldiers could then shoot at them. Phosgene, used later in the war, was far more lethal. When inhaled even in small amounts, HCl forms in the lungs, affecting what is called “dry land drowning” as lung tissue was destroyed. The limited number of survivors of phosgene attacks claim that small doses of it smell like newly mown hay, or fresh-cut wheat.

It is staggeringly ironic than that elemental chlorine is today used as an inexpensive antibacterial in water, and thus has saved countless people from a wide variety of diseases. Even more so that phosgene is used as a starting material for several very useful plastics, all of which are produced in large volumes.

2.1 Method of production

The reaction chemistry that illustrates the synthesis of phosgene is a deceptively simple addition reaction. It can be represented as

$$Cl_{2(g)} + CO_{(g)} \longrightarrow COCl_{2(g)}$$

This does not however give any details about the reaction conditions, which are important for optimal yield of phosgene. The two reactants are passed through activated carbon, sometimes called activated charcoal. This serves a catalytic role. Since the reaction is exothermic and usually runs at a temperature zone of 50–150 °C, the reactor is typically cooled during the process.

The chlorine reactant is produced as one of the three products in what is called the chlor-alkali process. The other products of this process are sodium hydroxide and hydrogen gas. Carbon monoxide is usually produced by the reaction of carbon dioxide and carbon at elevated temperatures.

2.2 Volume of production annually

It is difficult to put a number on phosgene production annually, because the chemical’s toxicity dictates that it is immediately used for the production of other commodity chemicals at the location at which it is generated. Because of its ability to be used as a chemical weapon, large producers must be reported to the Organization for the Prohibition of Chemical Weapons (Organization for the Prohibition of Chemical Weapons, 2014).

It is however possible to find the production figures for the more common isocyanates, which are produced from phosgene. Totaled, several million tons of the most common are produced annually.

2.3 Sales

Almost no phosgene is sold as a commodity chemical. Rather, most is produced at the site where it will be further used in the production of other commodity chemicals, such as diamines and isocyanates.

2.4 Uses

As mentioned, phosgene had an infamous debut, but has evolved into a highly useful starting material for several bulk, organic chemicals.

Today, the major use of phosgene is in the production of isocyanates, almost all of which are further used in the production of polyurethanes. While there are many isocyanates, methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are the two most commercially important, and thus the two that are made in the largest volumes. There are several large producers of MDI, including (in alphabetical order):

1. BASF, Germany
2. Bayer, USA
3. BorsodChem
4. Dow, USA
5. Huntsman
6. Nippon Polyurethane, Japan
7. OCI, South Korea
8. Yantai Wanhua, China, producing approximately 1.1 million tons (BASF Polyurethanes, 2014; Bayer Polyurethanes, 2014; BorsodChem, 2014; Dow, 2014; Huntsman Polyurethanes, 2014; Nippon Polyurethane Industry, 2013; OCI, 2013; Yantai Wanhua, 2013).

There are other, smaller producers as well (International Isocyanate Institute, 2013). For the past several years, roughly 5 million tons of isocyanates have been produced annually. The production of isocyanates is a matter of reacting an amine with phosgene. Generically, the reaction is as shown in Figure 2.1.

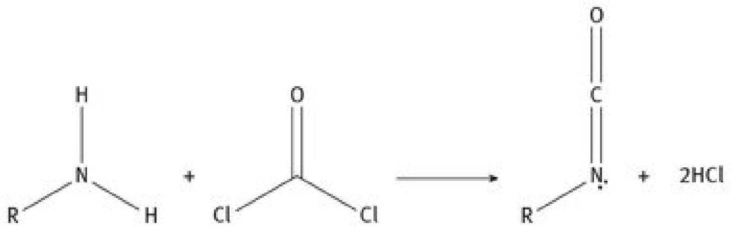

Fig. 2.1: Isocyanate production.

The more specific reaction to form MDI proceeds is shown in Figures 2.2 and 2.3.

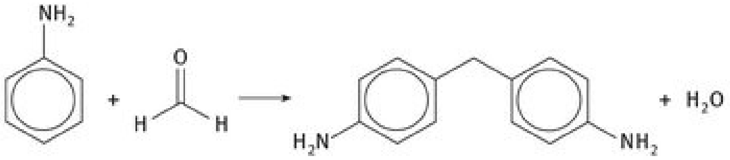

Fig. 2.2: Formation of methylene dianiline.

Aniline and formaldehyde form a precursor diamine. This is then reacted with 2 molar equivalents of phosgene to form the functional and reactive isocyanate ends, as seen in Figure 2.3.

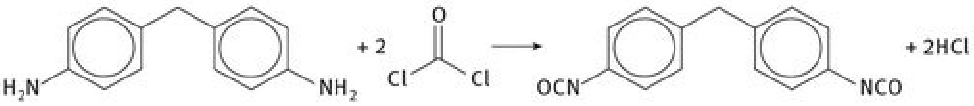

Fig. 2.3: MDI production.

In both cases, after the isocyanate has been formed, most are immediately converted to polyurethanes. The basic repeat unit for this is shown in Figure 2.4.

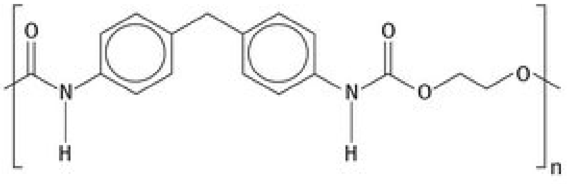

Fig. 2.4: Polyurethane repeat unit.

These diisocyanate units are reacted with a di-alcohol, generally called a diol. The resulting polymers, combinations of the isocyanate and alcohol, are polyurethanes, with the connecting −RN−CO_2 -unit, called carbamates. This becomes the final functional group. Polyurethanes have a wide variety of uses, but rigid, thermosetting polyurethane foams are used as insulating materials in refrigerators, freezers, and several other consumer end use products (Allport et al., 2003).

2.5 Recycling

As mentioned earlier, phosgene is almost always used at or near the site where it is produced. Thus, none exists for any sort of recycling or reuse. The end-product polyurethanes are recycled in cases where doing so is economically feasible. The American Chemistry Council website discusses the general ways in which such materials can be recycled (American Chemistry Council, 2014).

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3 Butyraldehyde

3.1 Method of production

There have been several methods for the production of butyraldehyde in the past (also known as butanal), including the dehydrogenation of butanol, but the dominant one today is propylene hydroformylation, often called the Oxo Process, as shown in Figure 3.1.

$$H_2C{=}CHCH_3 + CO_{(g)} + H_{2(g)} \rightarrow CH_3CH_2CH_2CHO$$

Fig. 3.1: Butyraldehyde production.

As mentioned in Chapter 2, carbon monoxide can be produced by the addition of carbon dioxide to carbon. Propylene is refined from the lighter fractions of crude oil. Hydrogen gas is often obtained by hydrocarbon stripping methane or other light hydrocarbons.

3.2 Volume of production annually

Each year, roughly 6 billion kilograms of butyraldehyde are produced. This figure has not changed appreciably in the past 5 years. All is consumed in further reactions, and little is sold as an end product. Because the material can be dangerous upon coming in contact with unprotected personnel, personal and environmental safety precautions are always taken, and almost all butyraldehyde is used at the site where it is generated.

3.3 Uses

Butyraldehyde has a wide profile of uses, akin to many of the large commodity chemicals produced across the world. The production of butanol and the production of 2-ethylhexanol for later use in the manufacture of phthalates are the two biggest uses, while niche uses incorporate everything from plastics components to solvent. While usage profiles from different companies will differ based on their customers, a recent profile from Dow Chemical Company appears in Figure 3.2 (Dow, 2013). Here we outline the uses of butyraldehyde in making these four products. Other uses are much smaller and are not listed here.

3.3.1 n-Butanol, production and uses

While an older method for the production of butyraldehyde began with n-butanol as a feedstock, today the reverse production is the case. Butyraldehyde is hydrogenated to form the alcohol (Dow, 2013). This will be discussed in more detail in Chapter 6.

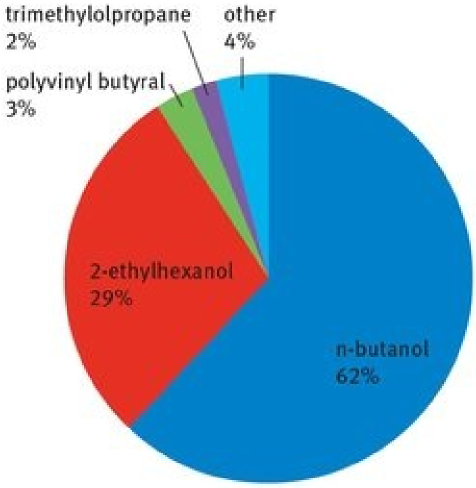

Fig. 3.2: Uses of butyraldehyde.

3.3.2 Uses of 2-ethylhexanol

2-Ethylhexanol can be produced in more than one way, but production usually involves a two-step process. What is sometimes called the Aldox process was perfected by Exxon and Royal Dutch Shell. The reactions are illustrated in Figure 3.3.

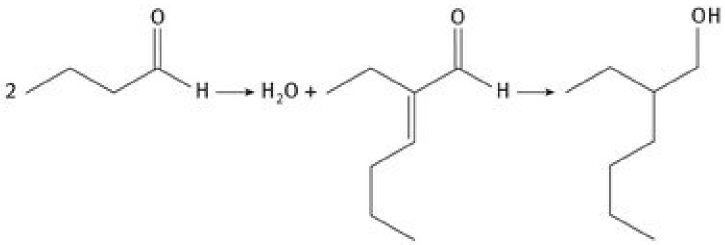

Fig. 3.3: 2-Ethylhexanol production.

The single use for virtually all 2-ethylhexanol is the production of the plasticizer: bis-(2-ethylhexyl) phthalate (usually abbreviated DEHP), which is shown in Figure 3.4. Phthalic anhydride is reacted with two moles of the alcohol resulting in the di-ester product and two moles of water as a by-product.

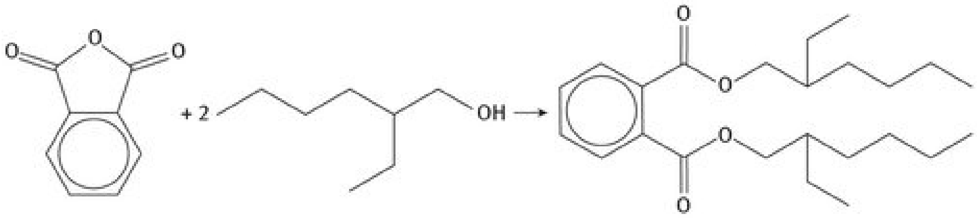

Fig. 3.4: Production of DEHP.

Since the 2-ethylhexanol has a chiral center, DEHP is produced with two chiral centers, and is sold as a mixture of the three different possible isomers.

This phthalate is used extensively as a plasticizer in several polymeric materials, most notable polyvinyl chloride (PVC), making the resultant materials more pliable and less brittle. Depending on the desired or required properties of a material, DEHP can be mixed to more than 35% by weight of the final product. It has also found use in some consumer-care products, such as sunscreens and lotions (UV Natural, 2014).

3.3.3 Uses of polyvinyl butyral

Polyvinyl butyral is a specialty plastic prepared from butyraldehyde and polyvinyl alcohol (sometimes called PVA). The reaction is shown in Figure 3.5.

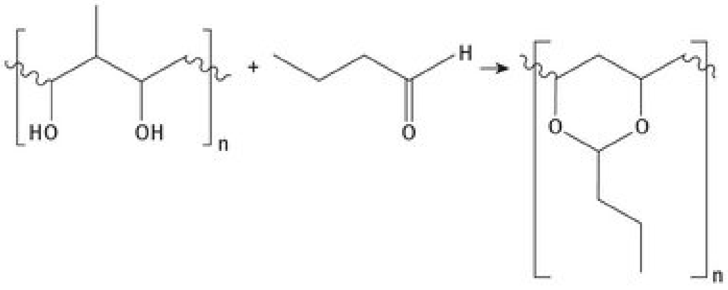

Fig. 3.5: Production of polyvinyl butyral.

By far the major use for polyvinyl butyral (sometimes abbreviated PVB) is the laminated type safety glass required in high strength applications such as automobiles and architectural window applications. Numerous trade names for this exist. They include:

– *Butacite* the DuPont trade name for PVB glass (DuPont, 2014).
– *GlasNovations* safety glass used in windows, doors, and automobiles (GlasNovations, 2014).
– *Saflex* Eastman trade name, safety glass used in numerous architectural applications (Eastman, 2014).
– *S-Lec* trade name for Sekisui interlaminate for automotive safety glass (Sekisui, 2014).
– *Trosifol* Kuraray, Ltd., the trade name for laminated glasses, mostly used in automotive applications (Kuraray, 2014).
– *WINLITE* PerryChem, trade name for laminated glass used in automotive and architectural applications (PerryChem, 2014).

3.3.4 Uses of trimethylolpropane

Trimethylolpropane is produced from butyraldehyde and formaldehyde. The process is generally a two-step one, as shown in Figure 3.6.

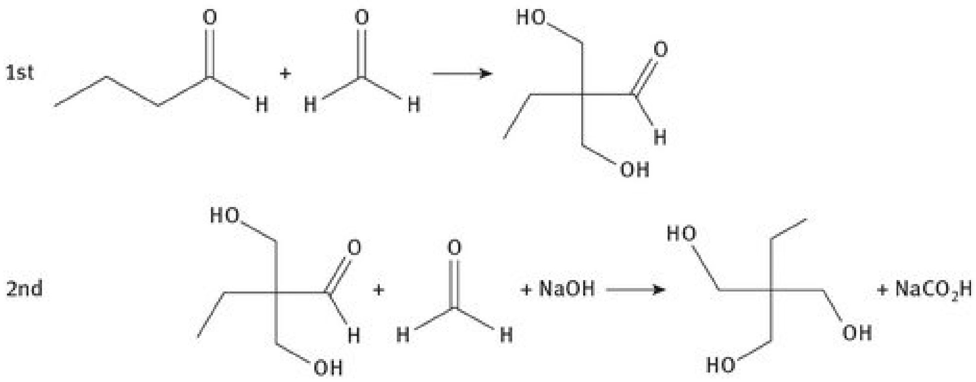

Fig. 3.6: Production of trimethylolpropane.

Sodium formate is the final by-product in the reaction. Trimethylolpropane is used in multiton quantities each year in the formation of alkyd resins – a class of polyesters – used for various applications, including multiple types of paints.

3.4 Recycling

We have seen that butyraldehyde is used completely in the production of other commodity chemicals. Thus, none is recycled. The four materials we have examined that are made with butyraldehyde are often used to create some user end-product or material. Thus, unless these materials are recycled, there is no second use for the butyraldehyde-containing material. Their use and disposal is often prescribed, discussed, or regulated through a Screening Information Dataset (SIDS), which is maintained by the Organization for Economic Cooperation and Development (OECD) (Organisation for Economic Cooperation and Development, 2013; OECD SIDS, 2013; OECD Existing Chemical Database, 2014).

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4 Acetic anhydride

4.1 Method of production

Acetic anhydride finds a large number of uses in the production of various commodity chemicals as well as in some consumer end products, such as aspirin and acetaminophen. It is manufactured from methyl acetate which in turn is made from methanol. Going back further, methanol is routinely produced from syn-gas, the combination of carbon monoxide and hydrogen gas in the presence of a metal or metal-oxide catalyst at elevated temperature and pressure (generally, 250 °C and 60–100 atm).

Thus, the reactions whereby acetic anhydride is produced from a single carbon atom source are shown in Figure 4.1. The final reaction requires rhodium iodide and lithium iodide as catalysts.

$$2\,H_{2(g)} + CO_{(g)} \rightarrow CH_3OH$$

$$CO_{(g)} + CH_3OH \rightarrow CH_3COOH \text{ and } CH_3COOCH_3$$

$$CO_{(g)} + CH_3COOCH_3 \rightarrow (CH_3CO)_2O$$

Fig. 4.1: Production of acetic anhydride from carbon monoxide.

The final reaction, shown in terms of Lewis structures, is shown in Figure 4.2.

Fig. 4.2: Acetic anhydride production from methyl acetate.

4.2 Production

The following companies are major manufacturers of acetic anhydride. By the names, it is evident that this material is produced widely across the globe, in a large number of countries.

Anhua Group

At their website (Anhua Group, 2014), Anhua states that it produces 80,000 metric tons of acetic anhydride annually.

BP

BP states at its website: “Over 75% of acetic anhydride is used in making cellulose acetate. It is found in filter tow, textiles, plastics, photographic, and X-ray film, and a diverse range of other applications. Acetic anhydride is used in the synthesis of a number of pharmaceuticals such as aspirin and paracetamol. It is also used in the manufacture of a bleach activator, which is extensively used in washing powder formulations” (BP, 2013, 2014). This statement and similar ones from other manufacturers confirm that the use of acetic anhydride for production of cellulose acetate is the primary use for this material.

Eastman Chemical

Eastman Chemical also produces acetic anhydride for a wide range of uses, including a kosher grade for food use (Eastman methyl acetate, 2013). Such high-grade material can be used for several modified starches, which in turn are given the numbers E1414, E1420, and E1422 by the International Starch Institute (International Starch Institute, 2014). E1414 is an aceytlated di-starch phosphate, E1420 is simply an acetylated starch with modification at the −OH, and E1422 is an acetylated starch that can also be described as a di-starch adipate. These and other modifications are designed to adjust such properties as viscosity and cold or hot water solubility of the product.

Celanese Chemicals

Celanese Chemicals, USA, also produces cellulose acetate as the major material from its acetic anhydride (Celanese, 2014).

Hoechst

Hoechst has an extensive history of using acetic anhydride in the production of acetaminophen (paracetamol), and pioneered the current process for its production.

IHS Chemical

IHS Chemical (2014) states at its website that: “Sixty-two percent of the acetic anhydride consumed globally in 2012 went to the production of cellulose acetate flake. Cellulose acetate flake, in turn, is converted to cigarette filter tow, filament yarns and plastics” (IHS Chemical, 2014).

Wacker-Chemie

Wacker-Chemie has been producing acetic anhydride for nearly a century, and developed the ketene process for its manufacture (Wacker, 2014; UNEP OECD SIDS, 2013).

4.3 Uses

While there are a variety of uses for this material, all of them acetylations, the reaction with cellulose to form cellulose acetate is generally the largest commercial application, as mentioned above. For example, this accounts for 75% of BP’s use of acetic anhydride, as mentioned above (BP, 2013, 2014). Most of the remainder is used in the production of aspirin and acetaminophen, the latter sometimes called paracetamol (BP, 2013, 2014).

Cellulose acetate finds use in photographic film coatings, cigarette filters, some diapers, as well as in other specialty coatings (see Figure 4.3). Apparently, Lego building blocks were made from cellulose acetate for several years starting in the late 1940’s.

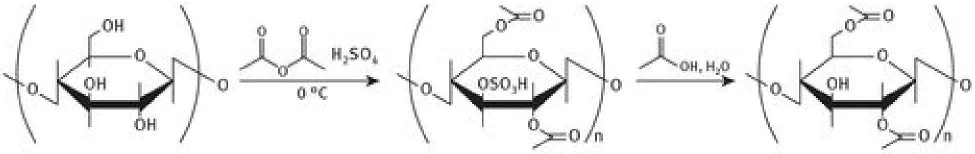

Fig. 4.3: Cellulose acetate production.

The production of aspirin is now a mature industry, but is one that requires a continuous input of acetic anhydride for the acetylation of salicylic acid (see Figure 4.4). In turn, the acid is produced from phenol, meaning that crude oil becomes the ultimate material source for aspirin.

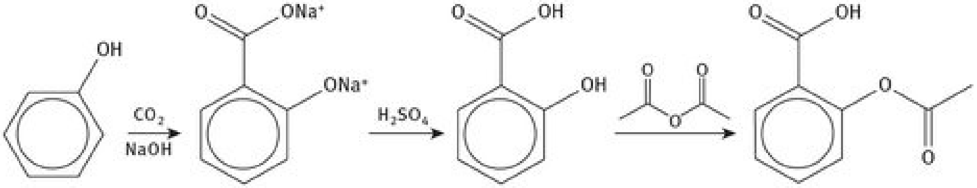

Fig. 4.4: Production of aspirin.

As can be seen from the production reactions for acetaminophen (see Figure 4.5), the starting materials are now ultimately oil once again, and hydrofluoric acid. Production and use of fluorine compounds are discussed in Chapter 22.

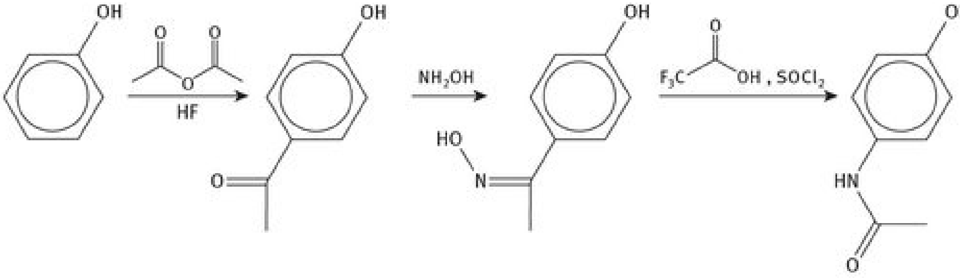

Fig. 4.5: Production of acetaminophen.

4.4 Recycling and reuse

All acetic anhydride is consumed in the production of other chemicals, and thus there are no recycling programs for it. There are also no large-scale recycling projects for the end-use products listed above.

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5 Linear alpha olefins (LAO)

The older term for a double bond, “olefin,” is still associated with this specialized series of organic, straight chain alkenes. Also, they are sometimes called normal alpha olefins; thus the abbreviations LAO and NAO are used interchangeably.

Although several different molecules fall into this category, all of the lower molecular weight LAOs have one basic use: to adjust the characteristics of the finished product when making polyethylene. Usually, an LAO is added as a co-monomer to produce low-density polyethylene (LDPE), although very small amounts of co-monomeric LAO can be used in the production of high-density polyethylene (HDPE). The higher molecular weight LAOs have a very broad application profile throughout different industries. Different ways to represent the general formula and structure for LAOs is shown in Figure 5.1, as is the representative example 1-octene.

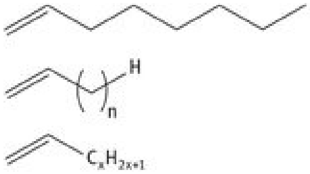


Fig. 5.1: Formula and structure of LAOs.

5.1 Methods of production

Several different companies produce LAOs, which means there are numerous small variations for the production of these materials. Broadly though, the production of LAOs is either done by the oligomerization of ethylene – the prime method – or by a Fischer–Tropsch synthesis, which must be followed by product separation and purification. The simplified reaction chemistry of ethylene oligomerization to 1-hexene (a material also sometimes called hexylene or butyl ethylene) is shown in Figure 5.2. Broadly, the process is similar up to materials such as 1-octadecene.

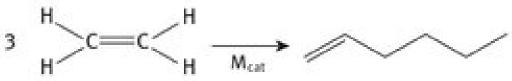


Fig. 5.2: Oligomerization of ethylene.

The oligomerization of ethylene is the main reason LAOs tend to be produced in even-numbered units (1-butene, 1-hexene, 1-octene, etc.), although odd numbered carbon chains are not impossible to produce. The following name processes are used for the production of LAOs:

1. Ethyl Corporation, or Ineos Process (Ineos, 2014)
2. Gulf Chevron Phillips Process (Chevron Phillips, 2014)
3. Idemitsu Petrochemical Process (Idemitsu, 2014)
4. IFP dimerization, used to produce 1-butene
5. Phillips ethylene trimerization process, used to produce 1-hexene exclusively (IHS, 2014)
6. SABIC-Linde Alpha-Sablin Process (SABIC-Linde Alpha-Sablin Process, 2014)
7. Shell Oil Company Process, or SHOP (Shell Oil Process, 2014).

The five companies and processes mentioned that are not noted for producing a single product produce a wide molecular weight distribution of LAOs, which can be separated so that specific product components can be put to different uses.

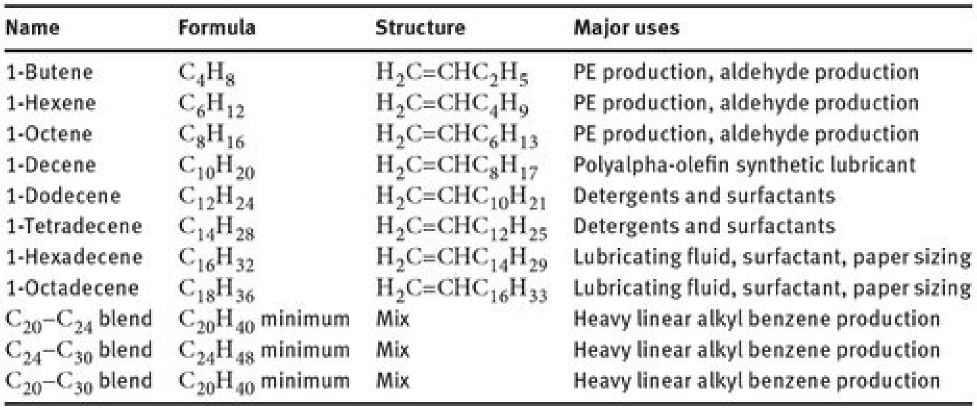
5.2 Uses of the different LAOs

The following linear alpha olefins in Table 5.1 find uses in various industries, although there are always niches for those not listed here, or for some of those that are listed, but for which there are smaller, secondary uses.

As seen above, linear alpha olefins have a wide profile of uses, depending on the molecular weight of the LAO in question. The lighter weight materials, specifically 1-butene, 1-hexene, and 1-octene, all find use almost exclusively to produce LDPE by increasing the branching as the polymer forms. Higher molecular weight materials can be used in widely different areas, though. Chevron Phillips, a major producer, states at their website:

"Normal alpha olefins, featuring highly accessible terminal double bonds, are ideal materials for manufacturing numerous products. Normal alpha olefins or their derivatives are used extensively as polyethylene co-monomers, plasticizers, synthetic motor oils, lubricants, automotive additives, surfactants, paper size, and in a wide range of specialty applications. As major petrochemical building blocks, their use in the development of new chemical products is virtually unlimited" (Chevron Phillips, 2014). The higher molecular weight LAOs find use as the "plasticizers, synthetic motor oils, lubricants" and other materials that are used to produce end products with specific viscosities and other desired characteristics.

Table 5.1: LAO formulae and uses.



Name	Formula	Structure	Major uses
1-Butene	C_4H_8	$H_2C{=}CHC_2H_5$	PE production, aldehyde production
1-Hexene	C_6H_{12}	$H_2C{=}CHC_4H_9$	PE production, aldehyde production
1-Octene	C_8H_{16}	$H_2C{=}CHC_6H_{13}$	PE production, aldehyde production
1-Decene	$C_{10}H_{20}$	$H_2C{=}CHC_8H_{17}$	Polyalpha-olefin synthetic lubricant
1-Dodecene	$C_{12}H_{24}$	$H_2C{=}CHC_{10}H_{21}$	Detergents and surfactants
1-Tetradecene	$C_{14}H_{28}$	$H_2C{=}CHC_{12}H_{25}$	Detergents and surfactants
1-Hexadecene	$C_{16}H_{32}$	$H_2C{=}CHC_{14}H_{29}$	Lubricating fluid, surfactant, paper sizing
1-Octadecene	$C_{18}H_{36}$	$H_2C{=}CHC_{16}H_{33}$	Lubricating fluid, surfactant, paper sizing
C_{20}–C_{24} blend	$C_{20}H_{40}$ minimum	Mix	Heavy linear alkyl benzene production
C_{24}–C_{30} blend	$C_{24}H_{48}$ minimum	Mix	Heavy linear alkyl benzene production
C_{20}–C_{30} blend	$C_{20}H_{40}$ minimum	Mix	Heavy linear alkyl benzene production

Paper sizing is one other use of the LAOs of C16–C18 chain length. This refers to creating paper surfaces that are water repellent enough that inks dry on the surface, and is not absorbed into the paper. The resistance to water that is exhibited by high-grade papers is a result of the added paper sizing. Absorbent papers, such as paper towels, are referred to as “unsized papers.”

5.3 Recycling and reuse

Since lighter LAOs are entirely used as starting materials for plastics, many of which are designed for robust performance and thus long life, any discussion of recycling is that of recycling of the plastics. Higher-molecular weight LAOs are routinely used in processes that do not recycle their end materials.

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6 *n*-Butanol (1-butanol or *n*-butyl alcohol)

The term “alcohol” is used by the general public either to denote the drinkable liquid, ethyl alcohol – a mild intoxicant – or to a lesser extent isopropyl alcohol, also known as rubbing alcohol. *n*-Butanol does form as a fermentation product in certain natural processes, but does so only to a small degree. However, the industrial synthesis of n-butanol has become a large process in the past few decades (now more than 1 million tons annually across the globe), placing this material routinely in the top 100 chemicals produced on an annual basis.

6.1 Method of production

While an older industrial scale method for the production of butyraldehyde, which was discussed in Chapter 3, began with n-butanol as the feedstock, today the reverse is the case. Butyraldehyde is hydrogenated to form the alcohol. The reaction chemistry appears to be rather simple, as shown in Figure 6.1.

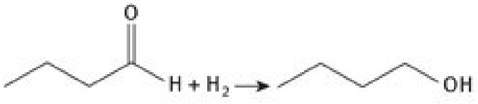

Fig. 6.1: Production of n-butanol.

This represents a significant large-scale use of hydrogen, most of which is produced from the hydrocarbon stripping of light hydrocarbons from natural gas or petroleum. However, the total amount of hydrogen used in *n*-butanol production is still far less than that consumed in the production of ammonia via the Haber process. Several different large chemical producers manufacture n-butanol. They include:

1. BASF (BASF (2014)) indicates at their website the broad profile of uses for which it manufactures n-butanol. It includes solvents for the coatings industry (about 50%), cellulose nitrate lacquers, as a diluent, alkyd resin paints additive to improve flow. Also
    - Solvent for dyes, *e.g.* in printing inks.
    - Extractant in the production of drugs and natural substances such as antibiotics, hormones, vitamins, alkaloids, and camphor.
    - Additive in polishes and cleaners, *e.g.* floor cleaners and stain removers.
    - Solubilizer in the textile industry, *e.g.* additive in spinning baths or carrier for coloring plastics.
    - Additive in de-icing fluids.
    - Additive in gasoline for spark-ignition engines (prevents carburetter icing).
    - Mobile phase in paper and thin-layer chromatography.
    - Humectant for cellulose nitrate.
    - Feedstock for the production of glycol ethers (in reaction with ethylene or propylene oxide) (BASF (2014)).
2. In Dow Chemical’s website (Dow Chemical, 2014), Dow indicates that 5.1 million metric tons of n-butanol were used worldwide in 2002.
3. Shivam Industries (2014) indicates not only its manufacture and sale of n-butanol, but of several commodity chemicals made from it.
4. Solvert (2014) indicates in its website that it focuses on “n-butanol, acetone, hydrogen, renewable energy.”
5. Ridhdhi Sidhdhi Chemicals (2014) markets n-butanol as a high purity solvent.
6. Ree Atharva Lifescience Pvt. Ltd. (Ree Atharva Lifescience Pvt Ltd, 2014) produces n-butanol in what it is called a pharma grade.

6.2 Uses

While it may seem surprising, n-butanol is referred to as a flavorant in its role as an additive to a variety of foods (OECD SIDS, 2013). The Organisation for Economic CoOperation and Development Screening Information Data Sets (OECD SIDS) states:

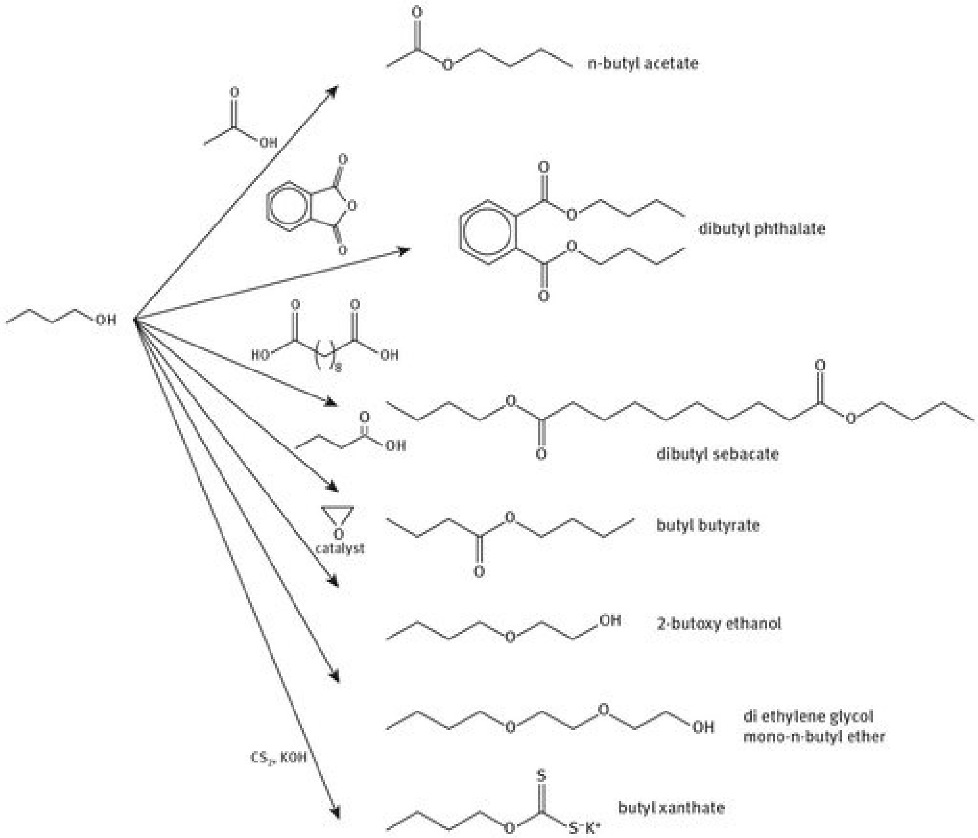

Fig. 6.2: Chemicals from n-butanol.

“In the United States, butyl alcohol is approved by the Federal Food and Drug Administration (FDA) as an indirect food additive for use only as a component of adhesives (21 CFR 175.105). It is a food additive permitted by the FDA for direction addition to food for human consumption (21 CFR 172.515)” (OECD SIDS, 2013).

n-Butanol has been approved for use in a wide variety of goods, from foods toto plastics to solvents. It is also used in the production of a wide variety of other commodity chemicals that in turn have widely differing end uses. Figure 6.2 shows the production of several other chemicals from n-butanol. Additionally, it is used in the manufacturing of materials as diverse as perfumes and vitamins, and is used in a variety of coatings and paints, as mentioned above.

6.3 Recycling and reuse

As mentioned, n-butanol is either used in end-use products or consumed in the production of other chemicals, so recycling is not possible.

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7 Methyl methacrylate

Several of the major, large-volume chemicals are produced on a large scale for later use in many different materials or consumer end products. Others, methyl methacrylate (MMA) included, tend to be produced for more limited purposes, although they are still produced on a very large scale. MMA is used predominantly for the production of the polymer, polymethyl methacrylate (PMMA), as well as for co-polymers. The reaction chemistry for the production of PMMA can be shown simply, as seen in Figure 7.1.

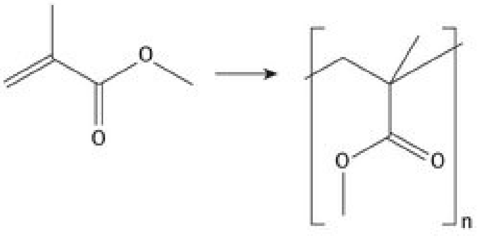

Fig. 7.1: PMMA synthesis.

7.1 Method of production

There is more than one method for the production of methyl methacrylate, but the largest has for some years been the acetone cyanohydrin method (ACH method), named after its starting materials.

7.1.1 The ACH method

The ACH production route for methyl methacrylate has been examined and its yields maximized over the years. Figure 7.2 shows the simplified reaction chemistry.

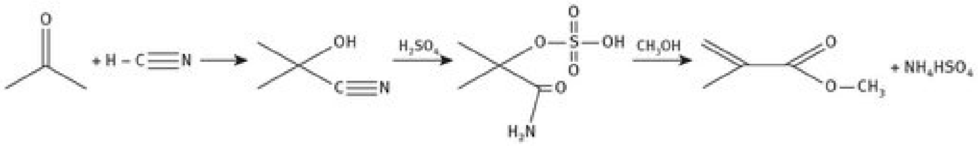

Fig. 7.2: ACH production of methyl methacrylate.

Acetone itself is produced industrially by the oxidation of cumene (isopropylbenzene), which co-produces phenol. Hydrogen cyanide is another chemical produced on a large scale annually, and is examined in Chapter 9. Sulfuric acid is the largest commodity chemical produced in the world, and in the United States it is produced in over 100 facilities within 29 states (United State Geological Survey, 2013). Methanol is yet another large commodity chemical, which is produced from syn gas. Methyl methacrylate production is only one of many uses for methanol.

Although this process is used to produce large quantities of methyl methacrylate, the ACH route also produces by-products in stoichiometric ratios. Specifically, ammonium hydrogen sulfate is a by-product that is always present in this process. Indeed, the production of 1 pound of methyl methacrylate through this process also produces approximately 2.5 pounds of the ammonium hydrogen sulfate. The disposal of this co-product becomes a serious concern.

7.1.2 Production from isobutylene

Isobutylene can be used as the starting material as well, and oxidized in air to produce methacrylic acid. The acid is then reacted with methanol to derive the product. The simplified reaction chemistry is shown in Figure 7.3.

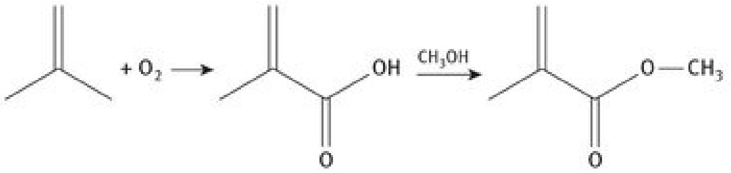

Fig. 7.3: Isobutylene production of methyl methacrylate.

Isobutylene itself can be separated from other light hydrocarbons that are present in natural gas.

7.1.3 Production from isobutyric acid

The production of isobutyric acid starts with propene (propylene), carbon monoxide, and water, and is catalyzed with hydrofluoric acid. Methacrylic acid is then produced from the isobutyric acid by dehydrogenation. Finally, the methyl group is added. The overall reaction chemistry is shown in Figure 7.4.

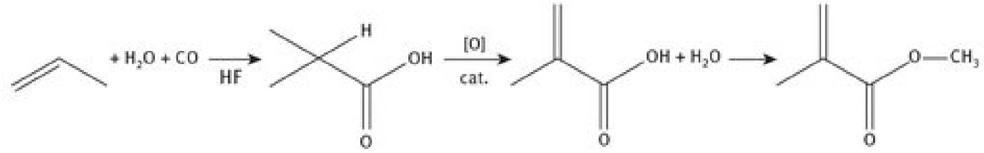

Fig. 7.4: Isobutyric acid production of methyl methacrylate.

Propene is another light hydrocarbon that ultimately has crude oil as its source material.

7.1.4 The methacrylonitrile process (MAN process)

Isobutylene is the main starting material for the MAN process, but the steps are different from those outlined in Section 7.1.2, above. Both ammonia and oxygen are required to produce methylacrylonitrile, which is then reacted with sulfuric acid to form a sulfuric acid adduct of the amide. The final step is the addition of methanol to form methyl methacrylate. The basic reaction chemistry is shown in Figure 7.5.

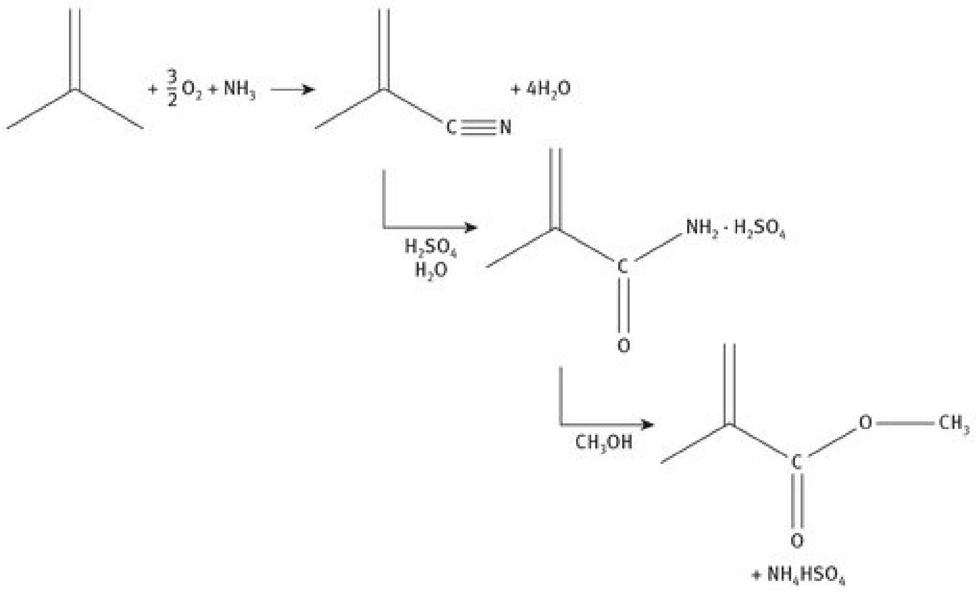

Fig. 7.5: MAN process for methyl methacrylate production.

7.1.5 Production from methyl propionate (the BASF Route)

This method begins with ethylene, and produces methyl propionate in the first step at slightly elevated pressure. The final step is the addition of formaldehyde to form the product. The simplified reaction chemistry is shown in Figure 7.6.

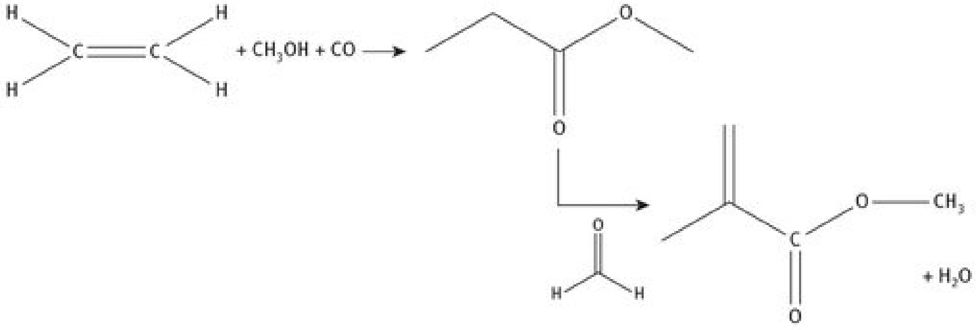

Fig. 7.6: Methyl propionate production of methyl methacrylate.

Ethylene is used in a large number of other applications, most notably the production of a variety of types of polyethylene, from linear low-density polyethylene to ultrahigh density polyethylene.

7.1.6 Production from propionaldehyde

In this synthesis, propanal (propionaldehyde) reacts with formaldehyde, using a secondary amine catalytically, resulting in methacrolein. This is then oxidized to form methacrylic acid. The acid is then converted to methyl methacrylate. The reaction chemistry for this is shown in Figure 7.7.

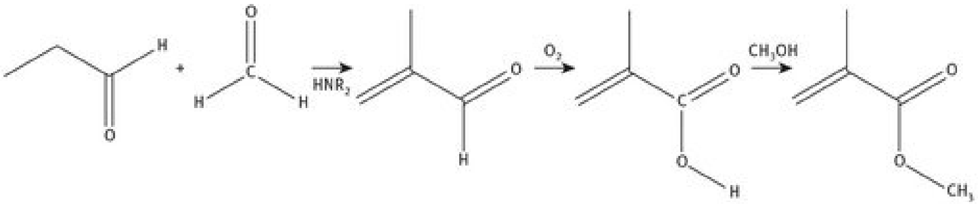

Fig. 7.7: Propionaldehyde production of methyl methacrylate.

Propanal is itself produced from ethylene in a hydroformylation. Again, the starting material is derived from a fraction of crude oil.

7.1.7 Production from propyne (aka, methyl acetylene)

In this process, propyne is reacted with both methanol and carbon monoxide using a metal catalyst and an acid. The reaction proceeds cleanly in a single step. The reaction is shown in Figure 7.8.

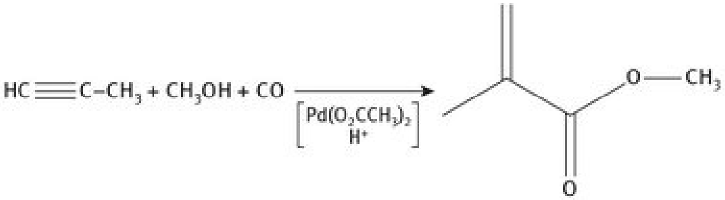

Fig. 7.8: Propyne production of methyl methacrylate.

Because this chemistry involves a metal catalyst and an acid, and proceeds at elevated pressures, it is often called Reppe chemistry, after pioneering chemist Walter Reppe, who worked extensively with various alkynes.

This series of synthetic pathways shows how wide the variety is in terms of how methyl methacrylate can be formed. Each synthesis is dependent on the availability and cost of its feedstock; but all the carbon-based molecules involved ultimately come from some fraction of petroleum.

7.2 Volume of production annually

The wide number of production routes to methyl methacrylate indicates that very large amounts are produced globally each year. One consulting firm that tracks the usage of large-scale chemical production and sales, Nexant, Inc., states

> At the end of 2008, there were almost 50 methyl methacrylate manufacturing plants globally (some uncertainty exists over the precise number of plants in China where the very small localized plants are scattered over a wide geography) with plant sizes ranging from 1500 to 360,000 metric tons per year (3.3 to 794 million pounds MMA per year) ChemSystems (2014).

This level of production generally appears to be steady from year to year, with some variations occurring, usually linked to the economies of the nations where it is produced.

7.3 Uses

Roughly three-fourths of all methyl methacrylate is used for the production of PMMA, as mentioned by Dow Chemical (2014). The polymerized PMMA structure is shown in Figure 7.9.

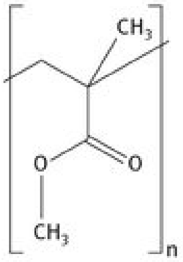

Fig. 7.9: Polymerized PMMA structure.

To a lesser extent, it is also used as a polymer material with butadiene and styrene (called MBS). This MBS ter-polymer, much like acrylonitrile-butadiene-styrene (or ABS) ter-polymer, is simply used to produce materials with desired properties, usually toughness, inertness, and proper flexibility or lack thereof for a specific application. MBS can be utilized to modify the properties of polyvinyl chloride (PVC), another large volume plastic. The MBS and ABS ter-polymer units are shown in Figure 7.10. There are other uses for methyl methacrylate as well. They include the following:

- Other methacrylate production
- Bone inserts
- Cement in joint replacements
- Acrylate polymers.

While production volumes do change each year, they have not done so drastically for the past several years.

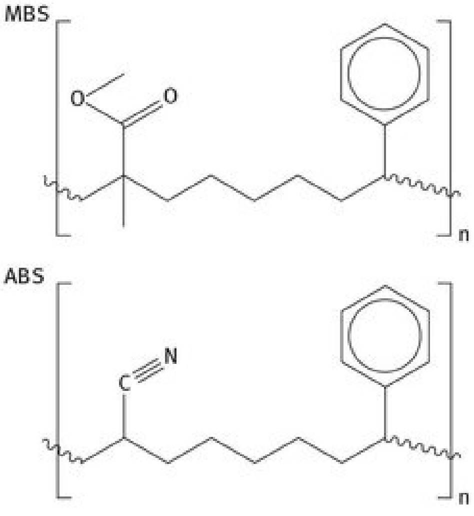

Fig. 7.10: The MBS and ABS ter-polymer repeat units.

7.4 Recycling and reuse

As with many plastics, recycling efforts for methyl methacrylate are not directed at the monomer, but rather for the polymerized material. Plastic production involves significant investments in material purity and in energy, and thus recycling is cost effective.

Since methyl methacrylate is essentially all consumed in the production of other chemicals and end-use materials, none of it is recycled.

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8 Hexamethylene diamine (HMDA)

Many of the large commodity organic chemicals produced today find many uses, sometimes in a wide variety of end-user products, and sometimes in a variety of different intermediate roles. Hexamethylene diamine (HMDA) is quite different in that its commercial use is almost exclusively in the manufacture of nylon-6,6, one of the most common types of nylon, with only small secondary uses (IHS Chemical, 2014; Solvay, 2014; Invista, 2014).

8.1 Method of production

HMDA has a long history, and through that time has been produced in different ways, at least on a small scale. Currently, it is produced from adiponitrile, the synthesis of which is shown in Figure 8.1

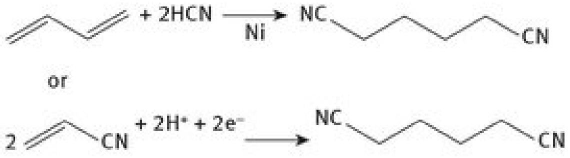

Fig. 8.1: Production of adiponitrile.

As can be seen, adiponitrile can be made in more than one way. But both methods shown in Figure 8.1 use starting materials – butadiene or acrylonitrile – that ultimately have petroleum as their source. The first method shown here has been pioneered by DuPont (DuPont, 2014) – which has been involved with the material deeply enough that two of its senior personnel have been entered in their Lavoisier Academy – and the second by Monsanto (Monsanto, 2014). The latter is an electrolytic process, which makes it energy intensive. The former requires a nickel catalyst to proceed to completion. The required hydrogen cyanide is the subject of the next chapter.

The final step that produces HMDA is the hydrogenation of the resulting adiponitrile, as shown in Figure 8.2.

Fig. 8.2: HMDA production from adiponitrile.

The reaction can be written in a very straightforward manner, but once again requires a catalyst for it to occur, usually an iron-based or cobalt-based catalyst. Also, there are side products that are isolated from the reaction, two of which are shown in Figure 8.3. The reaction is also a significant use for hydrogen.

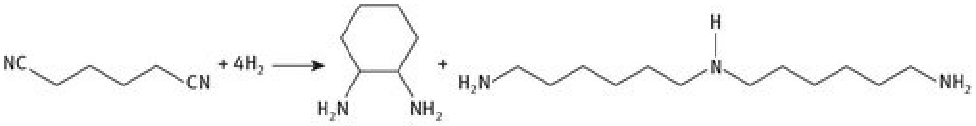

Fig. 8.3: By-product production during HMDA manufacture.

8.2 Volume of production and uses

Slightly more than 1 million tons of HMDA are produced annually. The vast majority of this is used in the production of plastics of one form or another. Perhaps the best known large scale use of it is for the production of nylon-6,6, this being a co-polymer with adipic acid. The chemistry can be represented in a straightforward manner, as is shown in Figure 8.4.

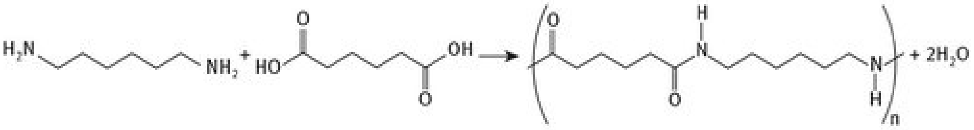

Fig. 8.4: Production of nylon-6,6.

Considerably less is used in the production of hexamethylene-diisocyanate. This latter material does find specialty applications though, usually in coatings.

Fig. 8.5: Production of isocyanate from HMDA.

These now classic syntheses have become sources of materials for a very wide variety of uses. Nylon can be spun into fibers of various gages, and used to create numerous durable fabrics for a multitude of end uses. It can also be shaped into a wide variety of consumer products or incorporated into them. Some of the most common are shown in Table 8.1.

Table 8.1: Nylon-6,6 uses.

Nylon-6,6 form	**Use**
Pellet, flake	Shaping or extrusion
Bulk material	Pipes, machine parts, auto parts
Fiber	Airbags, clothing, sails, rope, carpet, textile (Invista, 2014)
Fiber	Truck and bicycle tires, zip ties, flexible consumer products (Kolon, 2014)

8.3 Recycling and reuse

Since hexamethylene diamine is used almost entirely in the production of nylon, with other downstream products representing the rest of its use, the raw material is never reused or recycled.

Nylon and the other plastics made from HMDA can be recycled, and sometimes are. This usually depends on recycling laws in different states and provinces. In several parts of the world, tires are down scaled, meaning some second use is found for them, usually after their treads have been worn or compromised. Such uses include berm and dam material, or matting, after they have been mechanically shredded.

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Monsanto no longer displays any information related to such production on its website, and has refocused to agricultural products and chemicals.

Randall, D.; Lee, S. The Polyurethanes Book. Wiley, 2002, ISBN: 978-0-470-85041-1.

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9 Hydrogen cyanide (HCN)

The term “cyanide” sets off alarm bells with the general public, despite there being numerous positive uses for cyanide-containing materials. Popular culture often uses the term in movies and other forms of entertainment as a catch-all phrase for poison. Indeed, cyanide-containing compounds have been used in the 20th century in the arsenal of chemical weaponry, and it is classified as a blood agent. But as we will discuss, hydrogen cyanide is useful in several organic chemical transformations, and in the production of several chemicals that are produced on very large scales.

9.1 Method of production

Hydrogen cyanide production begins with methane and ammonia. Ammonia, for many years, has been a chemical produced in one of the two greatest amounts on Earth (the other is sulfuric acid). Methane is the major component of natural gas, and is extracted from natural gas wells throughout the world. The simplified reaction chemistry is shown in Figure 9.1.

$$2\,NH_3 + 2\,CH_4 + 3\,O_2 \rightarrow 2\,HCN + 6\,H_2O$$

Fig. 9.1: Hydrogen cyanide production.

Once again, the reaction does not provide all the necessary details, as this reaction requires a platinum catalyst and temperatures of approximately 1200 °C. Also, the reaction is exothermic enough that the heat generated by it is often used to help other reactions. This reaction is called the Andrussow Oxidation or Andrussow process, after its inventor, the chemical engineer Leonid Andrussow, who was working within IG Farben at the time of its discovery. Additionally, hydrogen cyanide can be made through what appears to be a more direct combination of methane and ammonia, as seen in Figure 9.2.

$$NH_3 + CH_4 \rightarrow HCN + 3\,H_2$$

Fig. 9.2: Direct combination of methane and ammonia for hydrogen cyanide production.

This is referred to both as the Degussa process, because Degussa is the firm that first developed it, as well as the BMA process which is an abbreviation of the German terms “Blausaeure, Methan, Ammoniak” (in English: hydrogen cyanide, methane, and ammonia). The process is endothermic, and historically has required platinum-coated piping and temperatures of about 1400 °C. Thus, it is not used to as large an extent as the Andrussow process.

The Shawinigan process is another electrolytic method of production of hydrogen cyanide. In this process, ammonia and propane are fed as a mixture over coke particles. While this produces yields of HCN over 80%, it runs at 1350–1650 °C, and thus is expensive in terms of energy.

9.2 Volume of production annually

Because of its poisonous nature, a great deal of hydrogen cyanide production occurs at or near the site where the material will be used further reaction chemistry so it does not need to be transported. Thus, it becomes difficult to put a number on the total amount produced annually, since this captive HCN is not usually counted. Additionally, any of the material that is stored by the military of any nation is generally not published or known, for reasons of security. However, estimates are that approximately 1 billion pounds of HCN are manufactured annually. At its website, IHS Chemical states

> In 2012, over fifty companies operated more than

> seventy hydrogen cyanide (HCN) production facilities in the world. Direct production accounts for about 68% of total capacity and the balance is derived as coproduct material from acrylonitrile production. DuPont had been the major global producer, with about 20% of this capacity, until it sold its fibers unit to Koch Industries, Inc. Koch now has about 14% of global capacity. Evonik–Degussa and Butachimie are also significant players, with about 8% and 10% of global capacity in 2012, respectively (IHS Chemical, 2014).

Clearly, HCN is manufactured and used on a large scale, and in a wide variety of uses and applications.

9.3 Uses

We have seen in Chapter 8 that HCN is used in the production of hexamethylene diamine, and thus in nylon. There are several other major uses, which are discussed in the following subsections.

9.3.1 Mining

Mining consumes a significant amount of cyanides, usually sodium and potassium cyanide, because cyanide has a high affinity for metal ions. When the metal is of high enough value, such as gold, it is economically worthwhile to use cyanide salts to capture the gold from any production and waste stream. The reaction chemistry by which sodium cyanide is produced is shown in Figure 9.3.

$$\mathrm{HCN + NaOH \rightarrow H_2O + NaCN}$$

Fig. 9.3: Sodium cyanide production.

It is perhaps obvious that this reaction also consumes a significant amount of sodium hydroxide, another chemical produced in large quantities annually. The reaction chemistry in which sodium cyanide reacts with gold is straightforward, as shown in Figure 9.4.

$$8\ NaCN + 4\ Au + O_2 + 2\ H_2O \rightarrow 4\ Na[Au(CN)_2] + 4\ NaOH$$

Fig. 9.4: Gold complexation by sodium cyanide.

It is this high affinity for the cyanide ion to gold that makes the reaction so important in extracting gold from deposits where it is a minor component. The process is highly efficient and cost effective. The production and use of potassium cyanide mirrors that of sodium cyanide.

9.3.2 Adiponitrile

This material is the precursor to hexamethylene diamine, and that to nylon-6,6, as discussed in Chapter 8.

9.3.3 Acetone cyanohydrin

This chemical is used in one of the methods of production for methyl methacrylate, and is shown in Figure 7.2.

9.3.4 Methionine

This amino acid is defined as an essential amino acid, meaning it is not produced in the body, and thus it is essential that it be consumed. The large-scale synthesis of methionine is shown in Figure 9.5, where it can be seen that potassium cyanide is a required reagent.

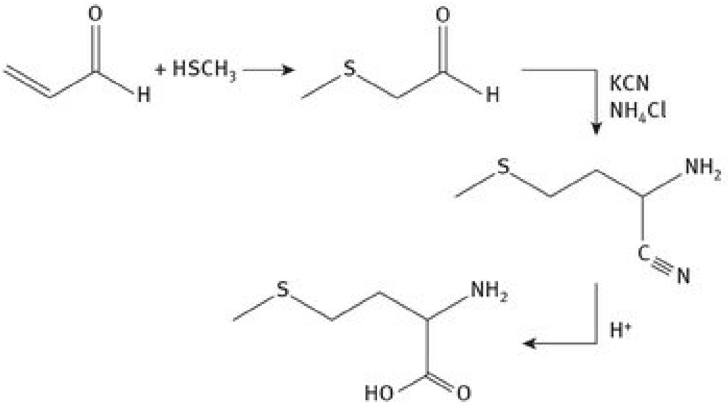

Fig. 9.5: Methionine production.

9.3.5 Cyanuric chloride and cyanogen chloride

The former of these two is prepared through the second as an intermediate compound. All of this is consumed in the production of the pesticide atrazine, an ethyl-isopropyl-derivative of $CNCl_3$. Over 100,000 tons have been produced annually for the past several years.

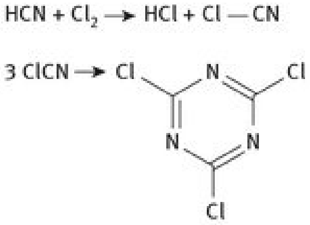

Fig. 9.6: Cyanuric chloride production.

9.3.6 Chelators

Hydrogen cyanide or sodium cyanide is also used in the production of the chelator ethylene diamine tetraacetic acid, commonly abbreviated as EDTA. The resulting EDTA or EDTA salt finds numerous uses in a wide variety of applications, such as metal ion sequestration in textile dyeing, or even in the paper and pulp industry. The synthesis is shown in Figure 9.7.

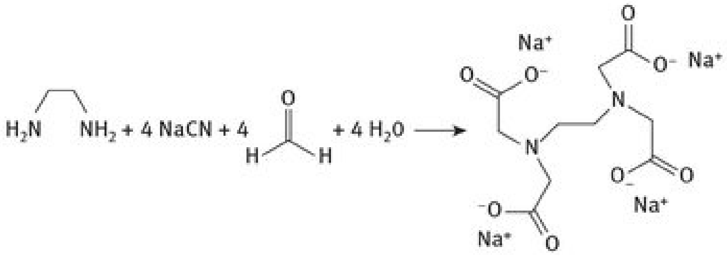

Fig. 9.7: EDTA production.

9.4 Recycling and reuse

Since hydrogen cyanide is never used as a material that is itself an end product, there is none that is recycled. However, since it is so poisonous, all industries that use the material have stringent safeguards in place to recover and reuse any HCN that is not consumed in the reaction. Releases of HCN are considered extremely dangerous, and thus every industry that uses it recovers all that does not react in some process.

The collection of different cyanide salts from mining waste streams is not a matter of recycling so much as a matter of containment. The liquid effluent and waste water from different mining operations can be very toxic, and containing it so that these materials are not released into the greater environment has become a matter of importance to governmental agencies, as well as to industries.

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cyanide.aspx)

10 Bisphenol A

Bisphenol A (so-called because the molecule incorporates two units of phenol and the carbon atoms from acetone) has been known for over a century, has had an industrial use since the 1950s and has been one of the top 100 chemicals produced globally for the past several decades. It has been used in the production of two broad categories of plastics and in food packaging plastics since shortly after the Second World War. Almost all bisphenol A finds use as monomeric material in plastics.

10.1 Method of production

Bisphenol A is produced from the reaction of two relatively simple, very inexpensive organic compounds, phenol and acetone, in a 2 : 1 molar ratio of phenol to acetone, as shown in Figure 10.1.

Both starting materials, phenol and acetone, are themselves made in what is sometimes called the cumene process or the Hock process, whereby benzene and propylene are reacted to form cumene (isopropyl benzene) at elevated temperature and pressure (generally 250 °C and 25–30 atm), then allowed to react with air, where the tertiary carbon–benzene bond is broken and combined with oxygen, yielding acetone and phenol. Indeed, this product mix can itself be used as a starting material for bisphenol A synthesis. Still, one can consider benzene and propylene as the ultimate refined, organic starting materials for bisphenol A. Both benzene and propylene are extracted from the crude oil.

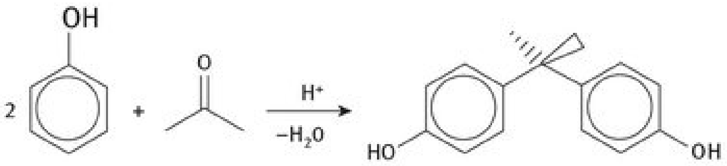

Fig. 10.1: Bisphenol A synthesis.

The reaction proceeds with acid catalysis, often hydrochloric acid, and is considered a condensation reaction, as the oxygen from acetone and the two para-positioned hydrogen atoms from each phenol unite to form water as the by-product. Usually, an excess of phenol is used to ensure optimum yields. The reaction does not always run cleanly, with minor, organic by-products forming, such as ortho-substituted products, and thus the final desired material is distilled from the product mixture.

10.2 Volume of production annually

For the past several years, over two million tons of bisphenol A have been produced annually. The production of bisphenol A has been on or near this scale for at least the past 20 years; with major industrial production going back to the 1950s. In general, future production appears slated to stay at or about at the same level.

There are several major producers of bisphenol A, including Dow Chemical, Bayer Polymers, SABIC, and Sunoco (ICIS, 2014; IHS, 2014). A fuller list includes the following, a set of globally diverse companies:

1. Anhui Shanfu New Material Technology Co., Ltd. (Anhui Shanfu, 2014)
2. Bayer Material Science Bayer Material Science (2014)
3. Dalian CR Science Development Co., Ltd. (Dalian CR, 2014)
4. Dow Chemical (Dow Chemical, 2014)
5. Go Yen Chemical Industries Co., Ltd. (Go Yen, 2014)
6. Hexion Specialty Chemicals (Hexion Specialty

Chemicals, 2014). Hexion claims at its website to be the world’s largest producer of thermosetting resins. Thus, bisphenol A should be a significant reactant and material needed for its resin production.

7. Jingjiang Concord Plastics Technology Co., Ltd. (Jingjiang Concord, 2014)
8. Oxford Lab Chem, India (Oxford Lab Chem, 2014)
9. SABIC (SABIC, 2014)
10. Shanghai Jorle Fine Chem. Co., Ltd. (Shanghai Jorle, 2014)
11. Sunoco (Sunoco, 2014)
12. Toronto Research Chemicals, Inc. (Toronto Research Chemicals, 2014)

10.3 Uses

10.3.1 Polycarbonate production

Almost all bisphenol A is utilized in the production of plastics. Perhaps the most simple is the production of what is called polycarbonate plastic, the reaction chemistry for which is shown in Figure 10.2. Polycarbonate, or PC, accounts for almost three-fourth of all bisphenol A use (ICIS, 2014; IHS, 2014).

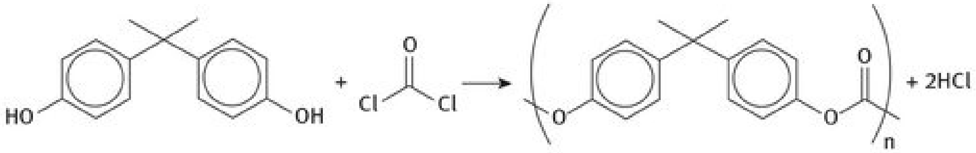

Fig. 10.2: Production of polycarbonate from bisphenol A.

The co-product, or by-product, of this synthesis is 2 molar equivalents of hydrochloric acid, which can be reclaimed or neutralized with a base.

The co-monomer in the synthesis, phosgene, is the subject of Chapter 2. Because of the highly toxic nature of phosgene, and because large volumes are required for the production of polycarbonate plastic on an industrial scale, diphenyl carbonate can be used as a co-monomer, as shown in Figure 10.3.

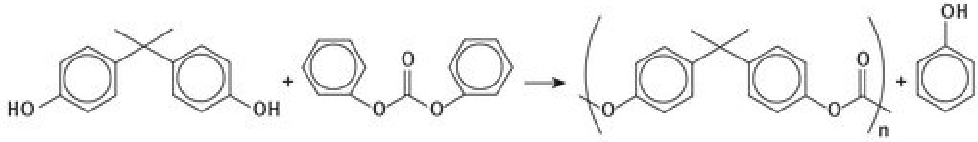

Fig. 10.3: Production of polycarbonate from bisphenol A and diphenyl carbonate.

The by-product of polycarbonate production when diphenyl carbonate is used as the co-monomer is phenol. Interestingly, in one method, phenol is made into diphenyl carbonate by the addition of phosgene. This means that while phosgene can be eliminated from the final production of polycarbonate, it may still be a reactant in an earlier reaction.

10.3.2 Epoxy resin production

Epoxy resins account for almost all of the remaining use of bisphenol A, comprising roughly 20% of total annual demand (ICIS, 2014; IHS, 2014). While several different kinds of epoxy resins exist, bisphenol A and epichlorohydrin are used to produce almost all of the epoxy resin that is commercially used. The simplified reaction chemistry is shown in Figure 10.4.

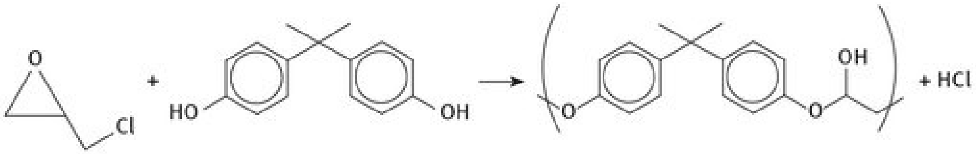

Fig. 10.4: Epoxy resin formation from bisphenol A and epichlorohydrin.

While the product is drawn as if it were simply one repeat unit in a polymer, the ratio of starting materials that make epoxy resins can be varied to adjust the final molecular weight, or molecular weight distribution, of the end product. Often, when a higher epichlorohydrin:bisphenol A ratio is used, the products are low molecular weight materials, sometimes called pre-polymers. As the ratio shifts to greater amounts of bisphenol A, the molecular weight or weight distribution of the product increases. These are considered to be linear polyether polymers.

Epoxy resins find numerous uses in a variety of consumer end products. Coatings, electric laminates, paving, and flooring are all examples. Perhaps the best known consumer end-use is that some adhesives are used for epoxy resins and glues.

10.4 The controversy

Bisphenol A continues to be a controversial material in terms of its use in food packaging plastics, because of its apparent role as an estrogen mimic, and because it is sometimes difficult to determine how much of a food contact material can enter into the food with which it comes into contact (for example, how much plastic wrap enters into food that is microwaved when still in the wrapper?). Calls have already been made to ban all use of bisphenol A, but the industry is mature and developed enough that this does not seem likely to occur.

Some products now produced without bisphenol A advertise this fact subtly, as shown in Figure 10.5. The figure shows a polycarbonate bottle, inverted, showing the resin identification code (RIC) of 7, and under the RIC recycle triangle the lettering “BPA FREE,” both molded into the plastic.

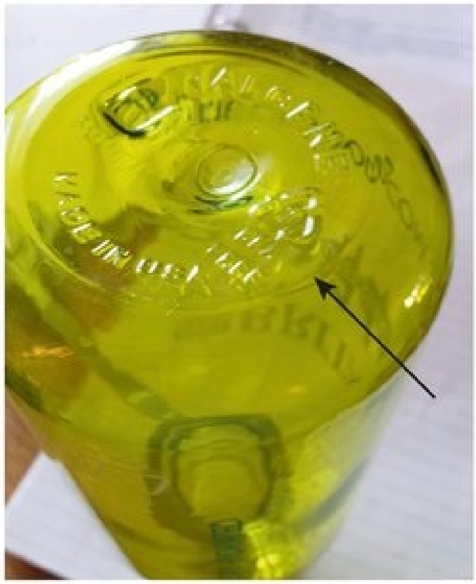

Fig. 10.5: BPA free beverage bottle.

10.5 Recycling and reuse

Any recycling with respect to bisphenol A is for the end product plastics into which it has been added or made, and not for the material itself. Thus, this form of reuse becomes part of the larger recycling programs instituted throughout different countries (BPA, 2014; Polycarbonate Recycling, 2014).

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11 Food additives

Any material intentionally put into food can be considered as food additive. Perhaps the oldest in history is the addition of salt, NaCl, which was used both to enhance flavor and to preserve foods for long periods of time when no form of artificial refrigeration was known, although vinegar may be a competitor for the title of "oldest." There are a few broad purposes for any food additive, such as enhancing color, flavor, or what is called "mouth feel." Also, additives to food are often used to preserve freshness and extend a product's shelf life.

11.1 Categorizing food additives: organic and inorganic

Food additives can be categorized in numerous ways and placed in several different subgroups. Since we wish to focus on the chemistry that goes into producing them, we begin by breaking this large field down into the broad categories of organic or inorganic materials. We will begin with several subdivisions of organic additives: food colorings, flavor enhancers, preservatives, and those that enhance mouth feel. This will be followed by a series of inorganic additives.

11.1.1 Food coloring

A wide variety of food colorings have been developed, which the United States Food and Drug Administration considers acceptable for human consumption. The term, "generally regarded as safe," (GRAS) applies to these substances.

As an example of food coloring use, Figure 11.1 shows the ingredients list from "Dippin' Dots Rainbow Ice Artificially Flavored Ice" which includes four different food colorings. While these are considered ingredients, they are specifically added to the material only to produce colors that are pleasing to the eye – so that consumers will purchase the item. Indeed, this is the purpose of many food colors – to make the food appear more palatable, or to give it a color the consumer expects or wants. Without such additives, many food items would not be as colorful as they are now, and would be perceived as less tasty. Other common examples are the famous M&Ms® and Skittles®.

Several food colors are currently in use in North America, the European Union, and other parts of the world. Others have been used, but are currently banned because of some safety and human health concern. Additionally, several colors have been developed and brought to large-scale production because they can be considered natural, and thus are perceived as being safer than colors that were those produced synthetically. Table 11.1 shows current food colors.

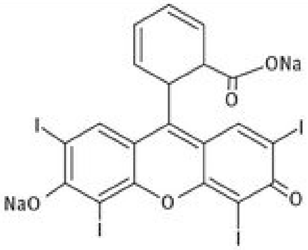
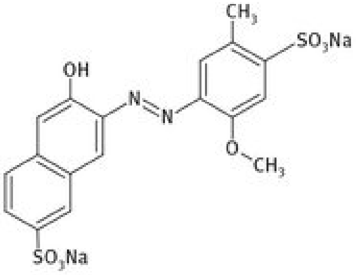
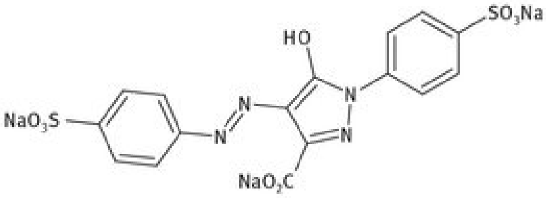
Ingredients: water, corn syrup, sucrose, artificial flavor, citric acid, yellow #6, yellow #5, red #40 and blue #1.

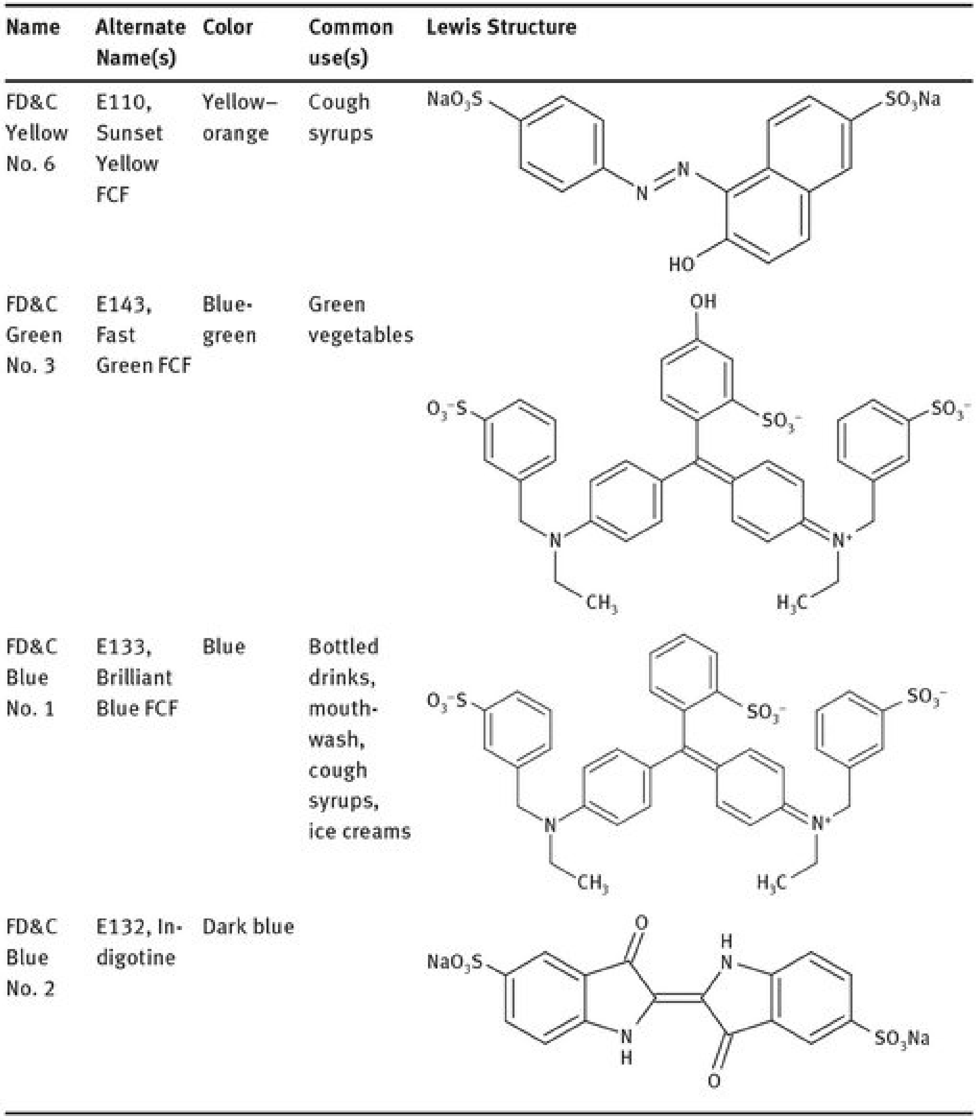
Manufactured and
Distributed by:
Dippin' Dots, LLC
(270) 443-8994
www.dippindots.com
Plant No. P21-240-2

Produced in a facility that contains milk, tree nut, wheat, soy & peanut products.

Fig. 11.1: Ingredients list from an ice cream product.

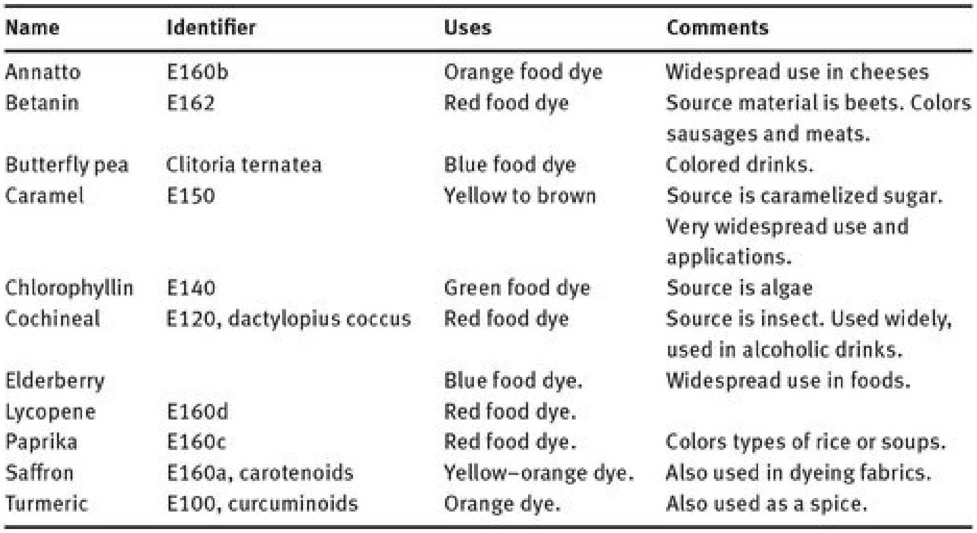
Table 11.1: Food colors in use (Food and Drug Administration, 2014).

Name	Alternate name(s)	Color	Common use(s)	Lewis Structure
FD&C Red No.3	E127, Erythrosine	Light red, pink	Cherries	
FD&C Red No.40	E129, Allura Red AC	Red	Ice cream, cough syrups	
FD&C Yellow No. 5	E102, Tartrazine	Yellow	Ice cream	



Name	Alternate Name(s)	Color	Common use(s)	Lewis Structure
FD&C Yellow No. 6	E110, Sunset Yellow FCF	Yellow–orange	Cough syrups	
FD&C Green No. 3	E143, Fast Green FCF	Blue-green	Green vegetables	
FD&C Blue No. 1	E133, Brilliant Blue FCF	Blue	Bottled drinks, mouth-wash, cough syrups, ice creams	
FD&C Blue No. 2	E132, In-digotine	Dark blue		

Table 11.2: Natural food colorings.



Name	Identifier	Uses	Comments
Annatto	E160b	Orange food dye	Widespread use in cheeses
Betanin	E162	Red food dye	Source material is beets. Colors sausages and meats.
Butterfly pea	Clitoria ternatea	Blue food dye	Colored drinks.
Caramel	E150	Yellow to brown	Source is caramelized sugar. Very widespread use and applications.
Chlorophyllin	E140	Green food dye	Source is algae
Cochineal	E120, dactylopius coccus	Red food dye	Source is insect. Used widely, used in alcoholic drinks.
Elderberry		Blue food dye.	Widespread use in foods.
Lycopene	E160d	Red food dye.	
Paprika	E160c	Red food dye.	Colors types of rice or soups.
Saffron	E160a, carotenoids	Yellow–orange dye.	Also used in dyeing fabrics.
Turmeric	E100, curcuminoids	Orange dye.	Also used as a spice.

What are called natural food colors are also regulated by the national government, since they are intended for human ingestion (Food and Drug Administration, 2014; Food Additives and Ingredients Association, 2014). A list of natural food colors is given in Table 11.2, although they are probably smaller, niche use food colors that are not listed here.

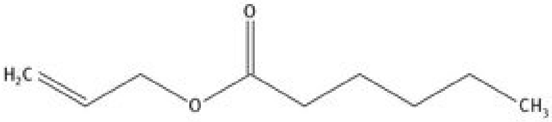
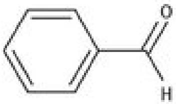
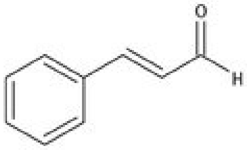
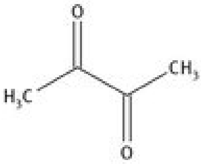
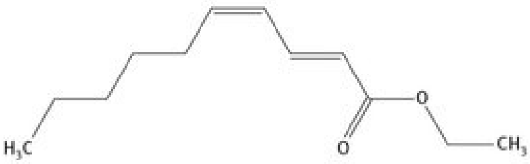
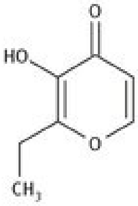
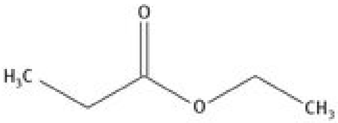
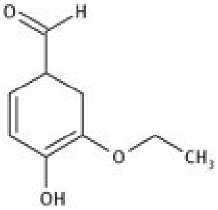
While colorings can be specific to foods, there are also several that can be used in other applications, which have been approved for use by the FDA (Food and Drug Administration, 2014). Saffron, mentioned in Table 11.2, is an example of a material that is also used in clothing dyes to impart a color that does not fade.

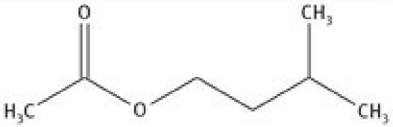
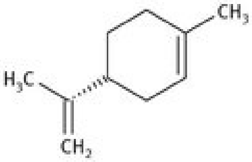
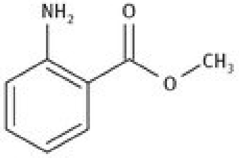
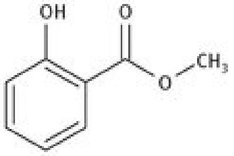
11.1.2 Flavor enhancers

By far, the oldest established flavor enhancers are salt and vinegar, known from ancient times. Perhaps this is followed historically by pepper and the other spices that came from Asia to Europe across the long land and sea trade routes during the Middle Ages. Indeed, this quest for rare and aromatic spices was one of the reasons a Genoese sailor at that time, Christobal Colon, was able to get royal endorsement to sail West from Europe to find the lands where these rare spices were produced. Now we know this man by his more anglicized name, Christopher Columbus.

Now, however, there are a variety of food additives recognized in the United States and Europe that qualify as flavor enhancers. Table 11.3 shows several of the more common flavor enhancers which are considered GRAS materials. There are others as well.

Table 11.3: Flavor enhancers.

Name	Other name(s)	Uses	Lewis structure
Allyl hexanoate		Pineapple	
Benzaldehyde		Almond	
Cinnamic aldehyde		Cinnamon	
Diacetyl	Butanedione	Butter	
Ethyl decadieneoate	Pear ester	Pear	
Ethyl maltol		Sugar	
Ethyl propionate		Fruit	
Ethyl vanillin		Vanilla, chocolate	

Name	Other name(s)	Uses	Lewis structure
Isoamyl acetate	Banana oil	Banana	
Limonene		Orange	
Methyl anthranilate	MA	Grape	
Methyl salicylate	Wintergreen oil	Wintergreen	
Salt	NaCl, Sea salt	Very widely used	Formula unit NaCl

It is notable that several of these structures are esters or aldehydes. Such molecules are often known for their pleasant fragrances (and sometimes unpleasant ones!). The large-scale synthesis of several of these materials now starts routinely with small organic molecules that have been separated from some fraction of crude oil. Examples of this are cinnamic aldehyde as shown in Figure 11.2 and wintergreen oil shown in Figure 11.3.

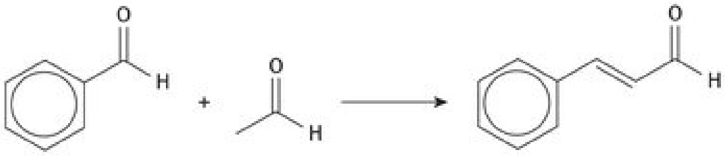


Fig. 11.2: Synthesis of cinnamic aldehyde.

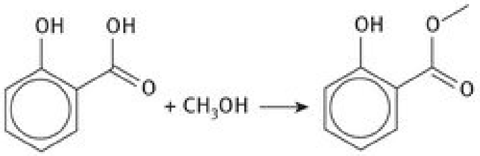


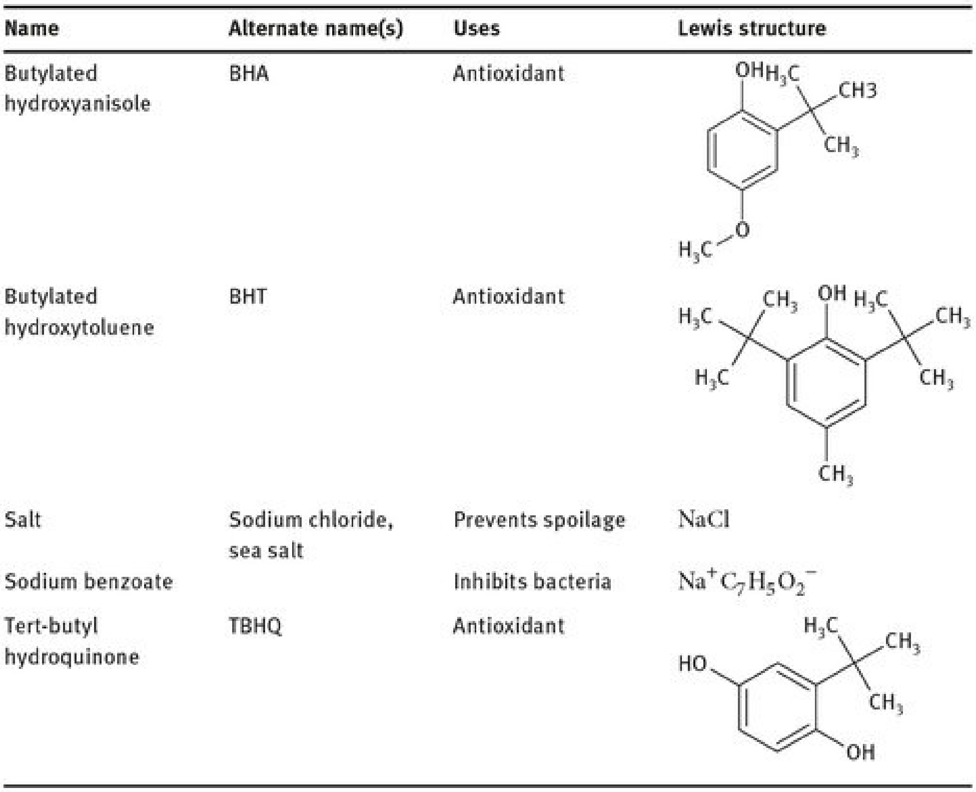
Fig. 11.3: Synthesis of wintergreen oil.

As can be seen from the starting materials in each of the above cases, the ultimate source for these two flavor enhancers is petroleum based, which means it will be abundantly available as long as petroleum is inexpensive.

11.1.3 Preserving freshness

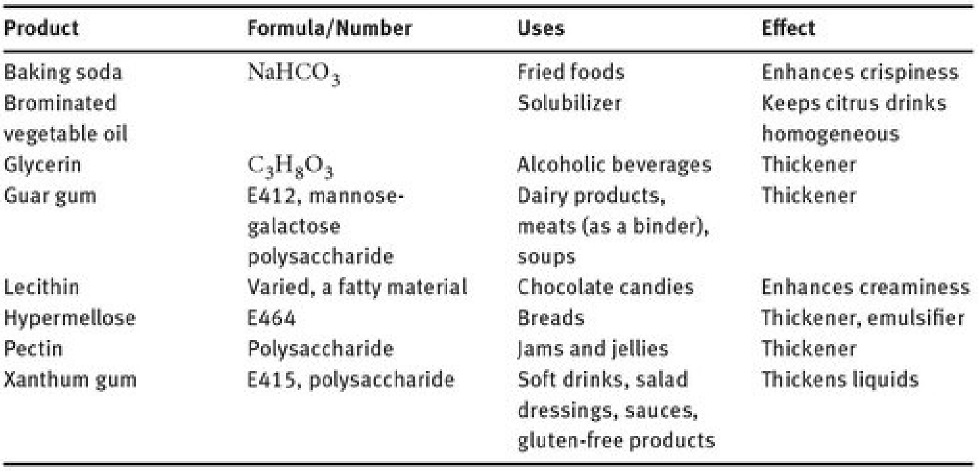
As with flavor enhancers, salt qualifies as one of the oldest food additives that have been used to preserve the freshness of foods. Since the Second World War, a number of additives have been discovered, and their production has been scaled up to industrial levels, which enable foods to be kept fresh for extended periods of time. This enables those foods to be transported long distances without spoilage. Table 11.4 lists the most common food preservatives.

Table 11.4: Common preservative food additives.



Name	Alternate name(s)	Uses	Lewis structure
Butylated hydroxyanisole	BHA	Antioxidant	
Butylated hydroxytoluene	BHT	Antioxidant	
Salt	Sodium chloride, sea salt	Prevents spoilage	$NaCl$
Sodium benzoate		Inhibits bacteria	$Na^+C_7H_5O_2^-$
Tert-butyl hydroquinone	TBHQ	Antioxidant	

Table 11.5: Food additives that enhance mouth feel.



Product	Formula/Number	Uses	Effect
Baking soda	$NaHCO_3$	Fried foods	Enhances crispiness
Brominated vegetable oil		Solubilizer	Keeps citrus drinks homogeneous
Glycerin	$C_3H_8O_3$	Alcoholic beverages	Thickener
Guar gum	E412, mannose-galactose polysaccharide	Dairy products, meats (as a binder), soups	Thickener
Lecithin	Varied, a fatty material	Chocolate candies	Enhances creaminess
Hypermellose	E464	Breads	Thickener, emulsifier
Pectin	Polysaccharide	Jams and jellies	Thickener
Xanthum gum	E415, polysaccharide	Soft drinks, salad dressings, sauces, gluten-free products	Thickens liquids

11.1.4 Enhancing mouth feel

The term “mouth feel” is rather self-explanatory. It is some material or substance that is designed to make an edible item feel more pleasant or agreeable while it is being consumed. There are many additives that serve this purpose. Once again, they must meet the safety requirements so that they can be considered as GRAS before they can be placed in products sold to the public. Some of the most common are listed in Table 11.5. These additives and several others are extracted from numerous plant sources. Often, when a product is sold as low calorie, some components are removed to lessen the total calorie count, and must be replaced to maintain the product’s volume. Additives that do this and enhance the mouth feel of the finished product thus, serve a dual purpose.

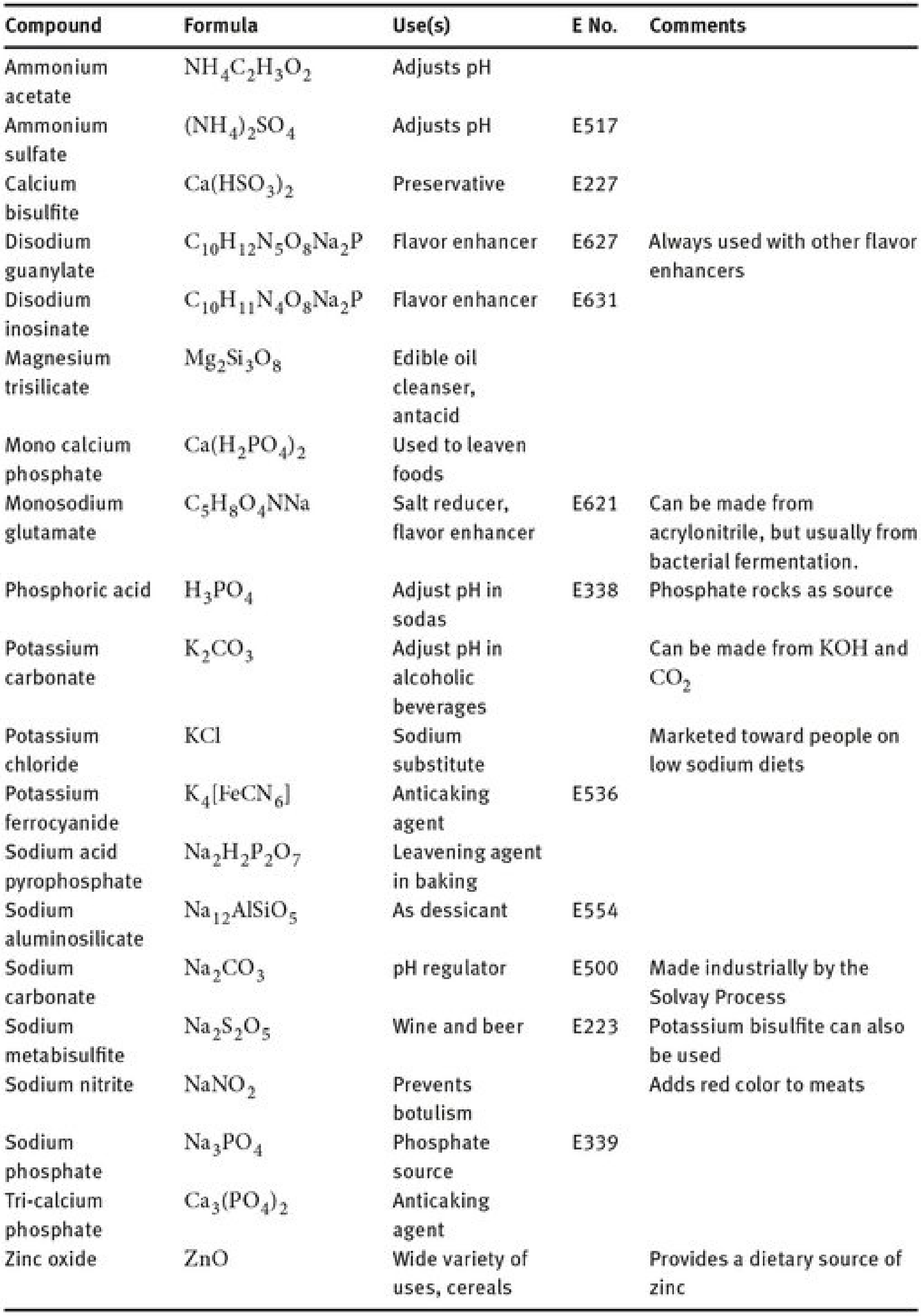
There is sometimes controversy when a synthetic mouth feel additive is incorporated into a food, as the idea of a synthetic additive appears to members of the general public to be unhealthy, or unnatural. In 2011, the addition of phthalates to some Taiwanese sports drinks raised concerns about the resultant health effects of consuming them (Self and Qu, 2012).

11.1.5 Inorganic additives

Numerous inorganic materials also find uses as food additives.

While we have listed common table salt in several of the above tables, there are several other inorganic materials which are added to foods. One can debate that some of these also qualify as organic, such as ammonium acetate, because while the ammonium may be inorganic, the acetate is an anion of an organic acid. Our listing in Table 11.6 shows several of the more commonly used materials, which have at least one inorganic component.

Table 11.6: Inorganic food additives.



Compound	Formula	Use(s)	E No.	Comments
Ammonium acetate	$NH_4C_2H_3O_2$	Adjusts pH		
Ammonium sulfate	$(NH_4)_2SO_4$	Adjusts pH	E517	
Calcium bisulfite	$Ca(HSO_3)_2$	Preservative	E227	
Disodium guanylate	$C_{10}H_{12}N_5O_8Na_2P$	Flavor enhancer	E627	Always used with other flavor enhancers
Disodium inosinate	$C_{10}H_{11}N_4O_8Na_2P$	Flavor enhancer	E631	
Magnesium trisilicate	$Mg_2Si_3O_8$	Edible oil cleanser, antacid		
Mono calcium phosphate	$Ca(H_2PO_4)_2$	Used to leaven foods		
Monosodium glutamate	$C_5H_8O_4NNa$	Salt reducer, flavor enhancer	E621	Can be made from acrylonitrile, but usually from bacterial fermentation.
Phosphoric acid	H_3PO_4	Adjust pH in sodas	E338	Phosphate rocks as source
Potassium carbonate	K_2CO_3	Adjust pH in alcoholic beverages		Can be made from KOH and CO_2
Potassium chloride	KCl	Sodium substitute		Marketed toward people on low sodium diets
Potassium ferrocyanide	$K_4[FeCN_6]$	Anticaking agent	E536	
Sodium acid pyrophosphate	$Na_2H_2P_2O_7$	Leavening agent in baking		
Sodium aluminosilicate	$Na_{12}AlSiO_5$	As dessicant	E554	
Sodium carbonate	Na_2CO_3	pH regulator	E500	Made industrially by the Solvay Process
Sodium metabisulfite	$Na_2S_2O_5$	Wine and beer	E223	Potassium bisulfite can also be used
Sodium nitrite	$NaNO_2$	Prevents botulism		Adds red color to meats
Sodium phosphate	Na_3PO_4	Phosphate source	E339	
Tri-calcium phosphate	$Ca_3(PO_4)_2$	Anticaking agent		
Zinc oxide	ZnO	Wide variety of uses, cereals		Provides a dietary source of zinc

11.2 Production

The methods by which food additives are produced on a large scale are more numerous than the number of additives themselves, as some have multiple production methods. For example, sodium chloride can be mined or reclaimed from ocean waters through evaporation of large and shallow pools.

Many organic materials, for example BHA and BHT, ultimately have oil as the source material. The production of BHT is shown in Figure 11.4 as an example, showing toluene as its starting material.

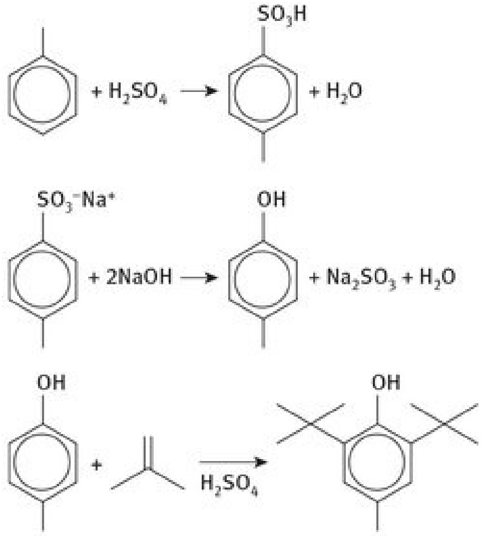


Fig. 11.4: BHT production.

Several inorganic materials that are used as food additives are produced from mining and refining a mineral source.

11.3 Recycling

Virtually none of the materials listed in this chapter are recycled. All are designed to be the part of one food product or another, and thus, they are consumed.

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Self, R. L.; Wu, W-H. Rapid qualitative analysis of phthalates added to food and nutraceutical products by direct analysis in real time/orbitrap mass spectrometry. *Food Control*, **25** (2012) 13–16.

12 Vitamins

Vitamins are generally small organic molecules that are essential for healthy life in most animals, including humans, always in small amounts. Although the knowledge that eating certain foods had health effects was known to some ancient cultures, their discovery, and understanding of them, really began only at the beginning of the 20th century – and indeed the complete understanding of the role of each of them is an ongoing field of study today. The earliest discoverers conjectured that these materials were all amines, and in the earliest publications the spelling of the word was often “vitamines,” a combination of vita and amines meaning living amines.

There are 13 recognized vitamins today, and several other materials that are sometimes referred to as “vitamin-like substances.” They are present not only in foods consumed by humans, but also in several different types of animal feeds. Trade organizations promote the safe use and consumption of vitamins (Natural Products Association, 2014; Vitamins.org, 2014).

12.1 Sources and production

All vitamins have numerous natural sources, and indeed were first isolated from some natural source. In many cases, plants are the source for vitamins, and humans and other animals have throughout history always eaten these plants to stay healthy. But some animals produce vitamins that other animals, humans included, must then ingest.

12.1.1 Vitamin A

As with several other vitamins, vitamin A is actually a group of related compounds that include several carotenoids, as well as retinal, retinol, and retinoic acid. The structure of retinol is shown in Figure 12.1.

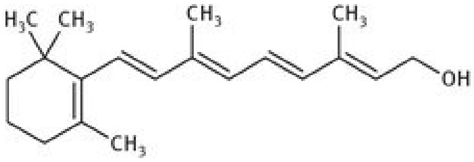


Fig. 12.1: Structure of retinol.

Vitamin A is fat soluble, and is found in many food products, both animal and vegetable. The following are high in vitamin A: cod liver oil; beef, chicken and turkey liver; carrots; dandelion greens; sweet potatoes.

The earliest work on the large scale, multistep synthesis of vitamin A was done by Hoffmann–La Roche, BASF, and Rhône–Poulenc. Hoffmann-La Roche sold its vitamins interests to DSM in 2003, and ultimately Rhône–Poulenc’s medicine and pharmaceutical operations became part of Bayer (Hoffmann-La Roche, 2014; Bayer, 2014; BASF, 2014).

12.1.2 Vitamin B_1

Vitamin B_1 is also known as thiamine or thiamin, and is classified as a water-soluble vitamin. Natural synthesis of thiamine is through plants, as well as through some bacteria and fungi. The Lewis structure of thiamine is shown in Figure 12.2.

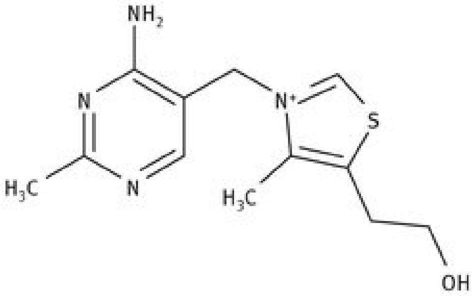


Fig. 12.2: Structure of thiamine.

The large-scale synthesis of thiamine has been pursued for decades, with Hoffmann–La Roche filing an early patent for a biologically based process (US Patent, 2014).

12.1.3 Vitamin B_2

Vitamin B_2 is also known as riboflavin, another water-soluble vitamin. It is found in a variety of animal and vegetable sources. Cheeses, meats, liver, and kidneys are animal sources that can be high in riboflavin. Almonds, mushrooms, and certain yeasts are other sources that are high in riboflavin. The Lewis structure is shown in Figure 12.3.

Vitamin B_2 can be produced on an industrial scale through the use of microbial systems and enzymes. Different companies may use different organisms, for example, BASF appears to utilize Ashbya gossypii exclusively, and produces riboflavin for both human consumption and animal feed (BASF, 2014).

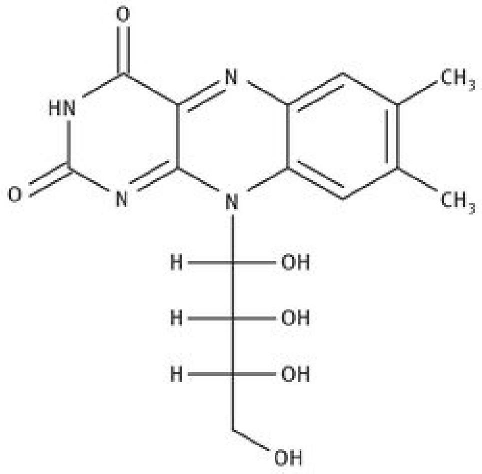


Fig. 12.3: Structure of riboflavin.

12.1.4 Vitamin B_3

Vitamin B_3 is also known as niacin, and is another water-soluble vitamin. It is found widely in animal and vegetable sources, including beef, chicken, and fish, as well as cereals and peanuts. The Lewis structure of it is shown in Figure 12.4.

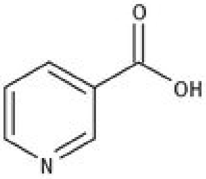


Fig. 12.4: Lewis Structure for niacin.

Niacin can be produced enzymatically from tryptophan, but can also be manufactured from 3-methylpyridine, which itself can be produced from acrolein and ammonia, as shown in Figure 12.5. Thus, the starting materials for this vitamin ultimately come from crude oil, as even the hydrogen in synthetic ammonia comes from fossil sources. Nearly 10 million tons of this vitamin are produced annually, with over half being consumed in animal feed.

12.1.5 Vitamin B_5

Vitamin B_5 is also called pantothenic acid, and is another water-soluble vitamin. It is found in most meats in at least small amounts, and is also found in whole grains. The Lewis structure and a representative synthesis are shown in Figure 12.6. Because of its presence in so many different plant and animal sources, diseases caused by its deficiency are rare.

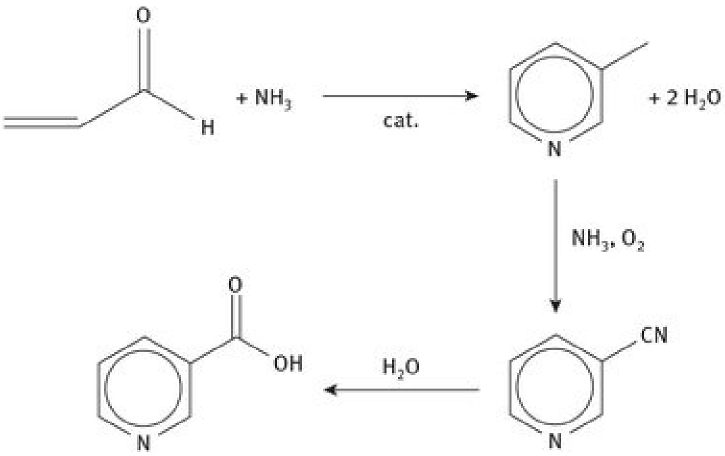


Fig. 12.5: Production of vitamin B_3

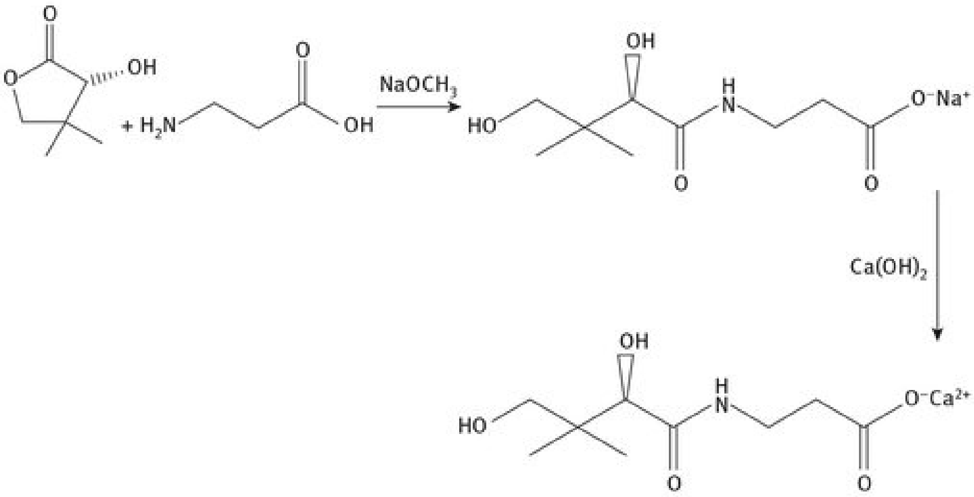


Fig. 12.6: Lewis structure and synthesis for pantothenic acid.

Several thousand tons of vitamin B_5 are produced annually, much for use in animal feed. In multivitamin supplements designed for human consumption, vitamin B_5 is often included as calcium pantothenate, its calcium salt. This is because the salt of the vitamin is stable over longer periods of time.

12.1.6 Vitamin B_6

Vitamin B_6 or pyridoxine is another water-soluble vitamin, in this case one which exists in seven different forms. The active form, pyridoxal phosphate (often abbreviated PLP) is shown in Figure 12.7.

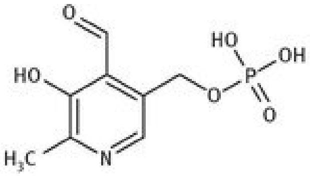


Fig. 12.7: Lewis structure of vitamin B_6

Vitamin B_6 is another material that is synthesized on a large scale using microbial and enzymatic processes. Some firms, such as Daiichi and Takeda, have developed different methods for the large-scale production of this vitamin (Daiichi, 2014; Takeda, 2014).

12.1.7 Vitamin B_7

Vitamin B_7 is another water-soluble vitamin, one that is also called biotin, or coenzyme R, or occasionally vitamin H. The Lewis structure is shown in Figure 12.8.

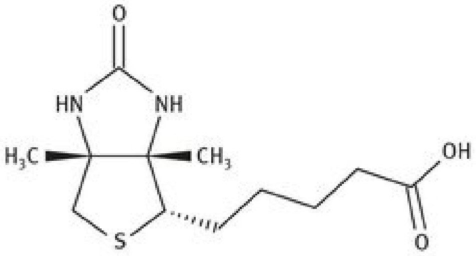


Fig. 12.8: Lewis structure of biotin.

The current synthesis of biotin, which produces the correct isomer, has not changed greatly from that developed by Hoffmann–La Roche in 1949, sometimes called the Sternbach–Goldberg synthesis. Fumaric acid is the starting material for this multistep process.

12.1.8 Vitamin B_9

Vitamin B_9 is another water-soluble vitamin, which is also called folic acid, folacin, or pteroyl-glutamic acid (and which has in the past been called vitamin M), all of which are much more useable terms than its IUPAC name: (2*S*)-2-[(4-{[(2-amino-4-hydroxypteridin-6-yl) methyl]amino}phenyl)formamido]pentanedioic acid. The Lewis structure is shown in Figure 12.9, as is one of its one-pot syntheses from three smaller starting materials.

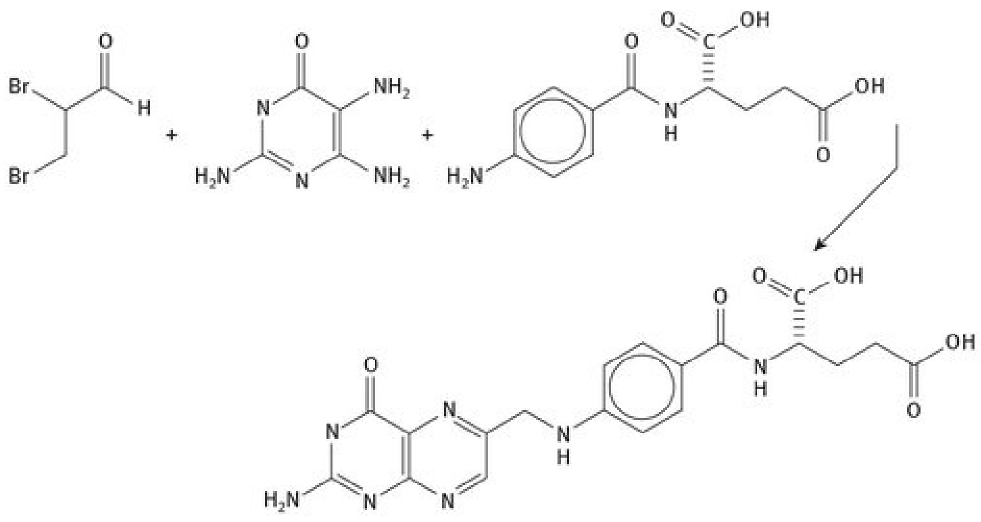


Fig. 12.9: Lewis structure and synthesis of folic acid.

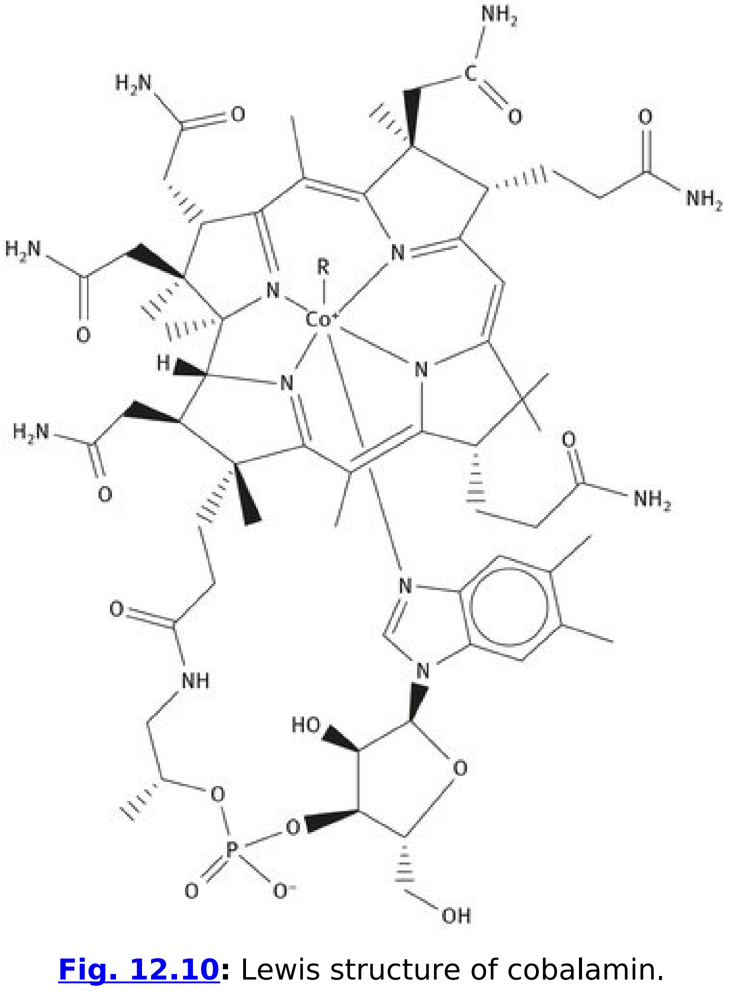


Fig. 12.10: Lewis structure of cobalamin.

12.1.9 Vitamin B_{12}

Vitamin B_{12}, also called cobalamin, is produced by different types of bacteria, and is not simply found in plant and animal sources. Its structure, shown in Figure 12.10,is the most complex of all the vitamins, and it was not discovered until 1954, by Professor Dorothy Hodgkin, who was awarded the Nobel Prize in Chemistry in 1964 for “her determinations by X-ray techniques of the structures of important biochemical substances” (NobelPrize.org, 2014).

The industrial scale production of vitamin B_{12} is still accomplished via a fermentation synthesis that is bacterially based. The organism *Psuedomonas dentrificans* is often used for large-scale production of this vitamin.

12.1.10 Vitamin C

Vitamin C is a water-soluble vitamin. Most people are familiar with the idea that citric fruits have significant amounts of vitamin C, and that it can easily be consumed by drinking orange juice. Oranges, lemons, and limes, in addition to several other plant sources, are high in this vitamin C. Its structure is shown in Figure 12.11.

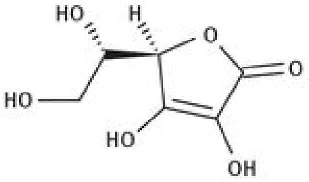


Fig. 12.11: Lewis structure of vitamin C.

The synthesis of vitamin C has been an industrial process for decades, and is often called the Reichstein process. BASF and Merck have been long-term producers of the vitamin. While it is a series of chemical steps, the use of acetobacter, as indicated in Figure 12.12, is crucial for ensuring the correct stereochemistry for all later steps. The final portion of vitamin C synthesis shown in Figure 12.12 is the equilibrium conversion between the open and closed structures of the active molecule.

12.1.11 Vitamin D

Vitamin D is a fat-soluble vitamin that can exist in several different forms, sometimes called vitamers. The broad term "vitamin D" generally refers to the forms that are more specifically called vitamin D_2 or vitamin D_3. The vitamin D_2 structure is shown in Figure 12.13.

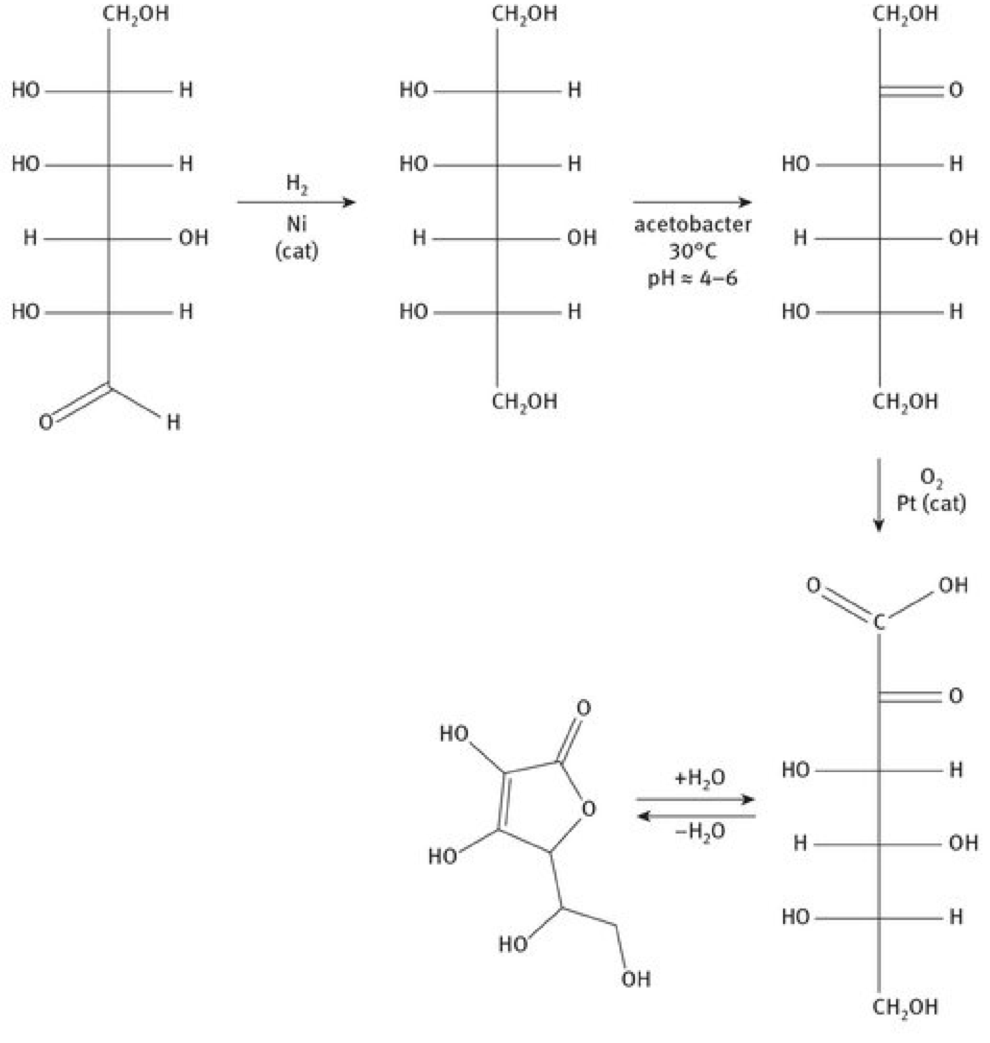


Fig. 12.12: Vitamin C synthesis.

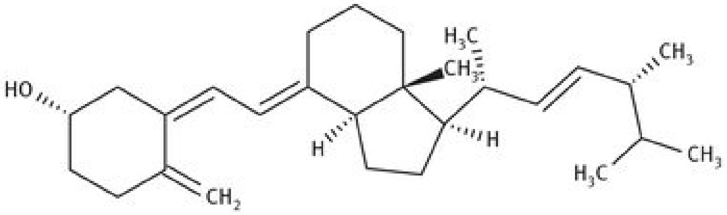


Fig. 12.13: Lewis structure of vitamin D_2.

Vitamin D_3 is synthesized in human skin from the action of ultraviolet light on a precursor molecule, 7-dehydrocholesterol. This molecule can in turn be extracted from lanolin (sometimes called “wool grease” or “wool wax”) if needed.

12.1.12 Vitamin E

The term vitamin E refers to a class of fat-soluble molecules that are all generally tocotrienols and tocopherols. The Lewis structure of the active form is shown in Figure 12.14, the form designated as alpha-tocopherol.

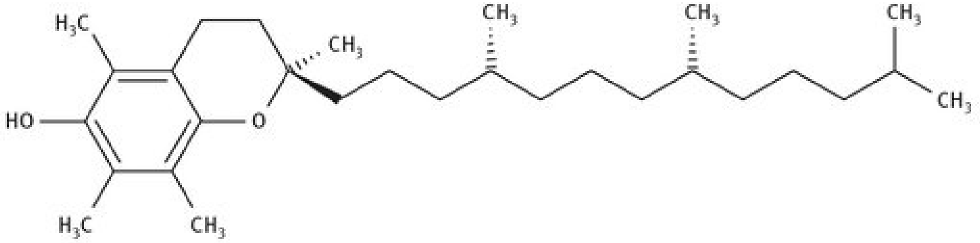


Fig. 12.14: Lewis structure of vitamin E.

Vitamin E can be divided into two groups of molecules, four of which are tocotrienols and four of which are tocopherols. There are three stereocenters in the molecules, and the R, R, R configuration of the tocopherols is the naturally occurring one.

There are different methods for vitamin E production, based on the company that produces it. Archer Daniels Midland claims at its website that “ADM has the broadest vitamin E product line, with alcohols, acetates and succinates in a wide range of manufacturer-friendly forms for capsule, tablet, and compounding applications. We offer powder formulations specifically designed for better flow and compressibility” (Archer Daniels MidlandI, 2014). Clearly, the production of what is called vitamin E is not that of a single molecule.

12.1.13 Vitamin K

Vitamin K has been known to be important to blood coagulation since its discovery in 1929. The term refers to a group of fat-soluble vitamins that are all structurally very similar. Figure 12.15 shows the structure of what is often called vitamin K_1, which occurs naturally in numerous leafy, green vegetables. The differences in the vitamin K often involve the length of the aliphatic chain. Large-scale production today usually involves the reaction of phytol (or another long chain alcohol) with menadiol. Both Merck and Roche have been active in producing vitamin K.

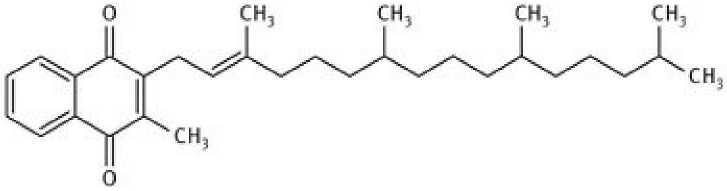


Fig. 12.15: Structure of vitamin K.

12.1.14 Vitamin F

The term “vitamin F” was used in the early part of the 20th century to describe what are now known to be two different fatty acids, called essential fatty acids because the human body does not synthesize them, but must ingest them. These two materials are alpha-linolenic acid and linoleic acid. The structure of each is shown in Figure 12.16.

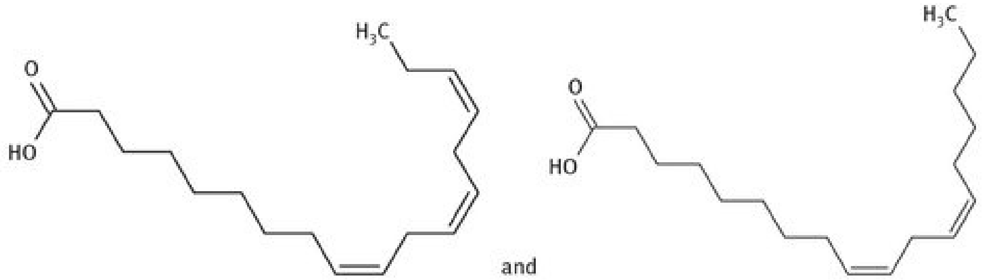


Fig. 12.16: Lewis structures of alpha-linolenic acid and linoleic acid.

The term vitamin F has fallen into disuse, however. These two molecules are now simply referred to as essential fatty acids, or EFAs. They are found in a variety of seeds, with kiwi and flax seeds being high in them.

12.2 Vitamin uses

Beyond simple requirements in human diets, and use as food additives in animal feed, vitamins find the following uses, listed in Table 12.1. Because lack of any vitamin in the human diet causes some disease of deficiency, vitamins fall under the US Food and Drug Administration designation of “generally recognized as safe,” (GRAS) and their addition to foods is usually not considered a problem.

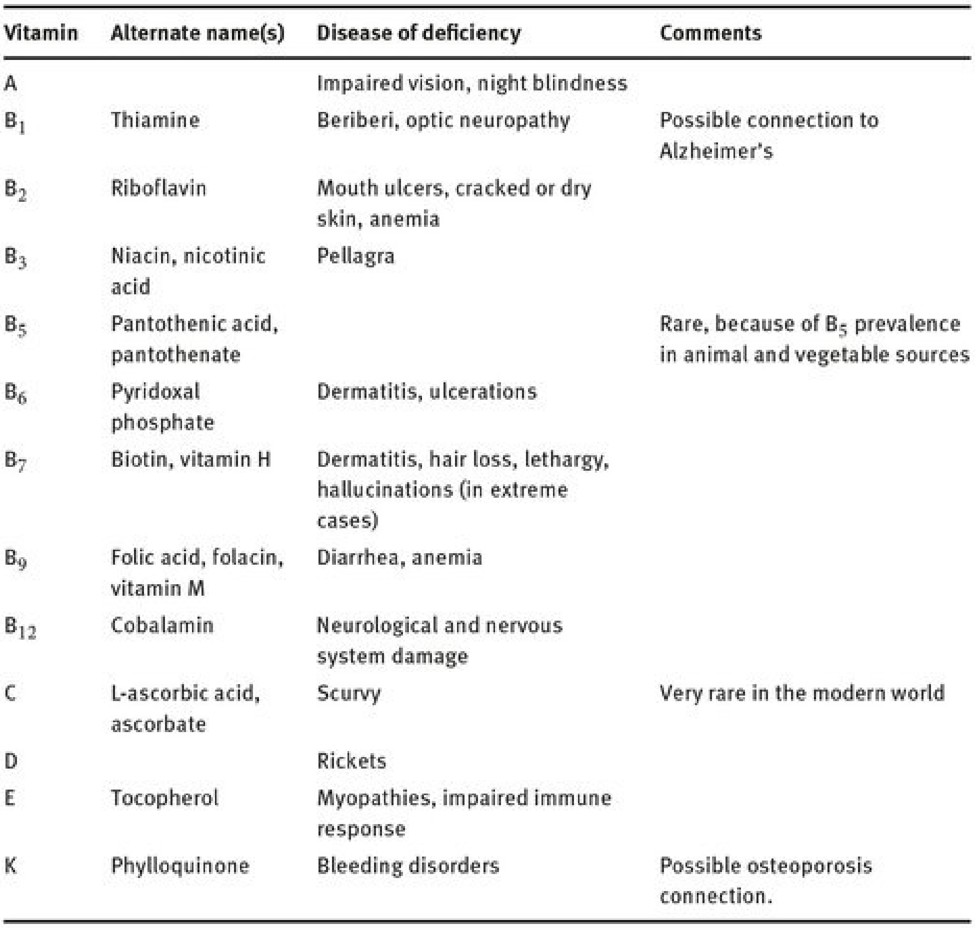
The role some vitamins play in human health continues to be an active area of study. Certain diseases of vitamin deficiency are well known to the general public, such as scurvy from a lack of vitamin C in the diet. Table 12.2 lists each vitamin and the disease to which a deficiency of it leads. But the uses and roles other vitamins play in human health, and how different dosages affect people, continue to be the subject of researchers’ interests.

Table 12.1: Vitamin use.

Vitamin	Use	Comments
A	Skin cream additive	

Riboflavin, B_2	Orange food coloring	Has the European number E101.
B_5	Shampoos	Appears to have no real effect on hair care
B_6	Antinausea during early pregnancy	
B_6 with magnesium	Treating autism	An alternative medicine choice, degree of effectiveness is still controversial
B_7	Protein assays	
B_{12}	Medical treatment for cyanide poisoning	
C	Food additive	Despite being prevalent in citrus fruits, vitamin C is added to numerous foods.

Table 12.2: Vitamins and diseases of deficiency.



Vitamin	Alternate name(s)	Disease of deficiency	Comments
A		Impaired vision, night blindness	
B_1	Thiamine	Beriberi, optic neuropathy	Possible connection to Alzheimer's
B_2	Riboflavin	Mouth ulcers, cracked or dry skin, anemia	
B_3	Niacin, nicotinic acid	Pellagra	
B_5	Pantothenic acid, pantothenate		Rare, because of B_5 prevalence in animal and vegetable sources
B_6	Pyridoxal phosphate	Dermatitis, ulcerations	
B_7	Biotin, vitamin H	Dermatitis, hair loss, lethargy, hallucinations (in extreme cases)	
B_9	Folic acid, folacin, vitamin M	Diarrhea, anemia	
B_{12}	Cobalamin	Neurological and nervous system damage	
C	L-ascorbic acid, ascorbate	Scurvy	Very rare in the modern world
D		Rickets	
E	Tocopherol	Myopathies, impaired immune response	
K	Phylloquinone	Bleeding disorders	Possible osteoporosis connection.

12.3 Recycling

Vitamins are consumed in some way, and thus there is no form of vitamin recycling either industrially or at the consumer level. In the past decade, some localities have instituted voluntary drug and medication return programs, which can include vitamin pills. The idea behind such programs is usually to prevent the introduction of medications, vitamins, and other such substances into local waters. Sewage treatment plants have traditionally not been designed to be able to remove these materials from water.

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13 Hydrogen peroxide

Hydrogen peroxide is the simplest of all the peroxides, and is produced each year on a scale of roughly 2 million tons. It has been considered a useful chemical in several different processes for over a century. Its production today is through an ingenious process, generally called the anthraquinone process, although it is sometimes referred to as the Riedl–Pfleiderer process. The process dates back to the 1930s and was pioneered at BASF (The Manufacture of Hydrogen Peroxide, 2014; BASF/Dow/Solvay, 2014).

13.1 Production

The anthraquinone process is currently the only industrial-scale process for the production of hydrogen peroxide (BASF/Dow/Solvay, 2014). The reaction chemistry is fascinating, but can be reduced to the deceptively simple, single reaction:

$$H_{2(g)} + O_{2(g)} \longrightarrow H_2O_2$$

The reason this simplicity is considered deceptive is the means by which the hydrogen and oxygen are reacted and joined: the anthraquinone. Figure 13.1 shows the catalytic and cyclic nature of hydrogen peroxide’s production.

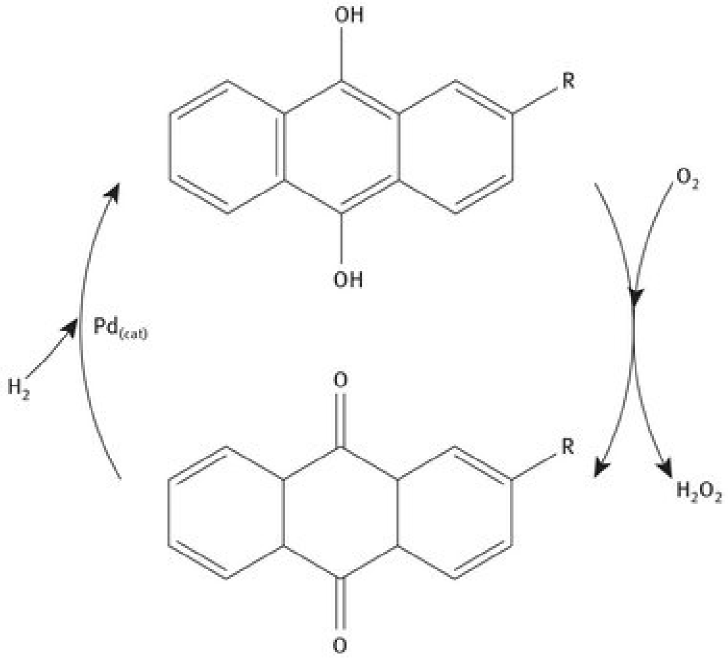

Fig. 13.1: The anthraquinone process.

The R group on the anthraquinone can be different alkyl groups, but ethyl is the most commonly used, with tert-butyl being another proven group. Putting the entire process into somewhat more detail and explaining the chemical reactions includes the following four major steps:

1. *Hydrogenation*. Molecular hydrogen is introduced to the anthraquinone with a palladium catalyst, producing anthrahydroquinone.
2. *Catalyst separation*. Because the palladium catalyst is denser than all other components involved in the process, it is filtered out, recovered and reused.
3. *Air input*. This oxidation step is the point at which oxygen from air is introduced to the process. Air is the least expensive component in the process and produces the oxidation.
4. *Product separation*. The hydrogen peroxide and anthraquinone are separated using an extraction column and the anthraquinone is reused.

There are times when more anthraquinone is added to the system, but for the most part it is recycled. Its purpose is to transport the hydrogen. At the BASF website, the process is explained as follows:

> The manufacturing process involves the catalysis of the reaction of H_2 (obtained from processing Maui gas) with atmospheric O_2 to give H_2O_2. Anthraquinone (Q) is used as a H_2 carrier. The major uses of peroxide in New Zealand utilize its strongly oxidizing nature to oxidize various chemical groups.
> During the hydrogenation step of hydrogen peroxide production, the working solution containing the dissolved anthraquinone is hydrogenated using hydrogen gas in a slurry-type hydrogenator using alumina loaded with a small amount of palladium catalyst. The anthraquinone working solution is heated in the presence of either activated alumina or activated magnesia, thereby regenerating its hydrogen peroxide synthesizing capacity (BASF/Dow/Solvay, 2014; BASF, 2014).

So, not only is palladium used catalytically and recycled, but also alumina or magnesia must be used as a support.

Because of the size of hydrogen peroxide production facilities, they must be located near a source of water, which must itself be further purified. Also, they can be co-located with a facility that produces hydrogen gas.

13.2 Uses of hydrogen peroxide

The general public tends to think of hydrogen peroxide as a treatment for minor scrapes and cuts, and think of the bottle of 1% H_2O_2 solution in a household medicine cabinet as the primary use for the material. While this is indeed one use for hydrogen peroxide, its profile of uses is quite wide.

Hydrogen peroxide is always miscible in water in any proportion, and is often sold as solutions of various concentrations. US Peroxide lists the following industrial applications of this material:

- Refinery and petrochemical reduced sulfur compound treatment
- Refinery and petrochemical supplemental dissolved oxygen
- Refinery and petrochemical high strength wastewater pretreatment
- Nitrogen oxides (NOx) abatement
- Cooling and process water system
- Antimicrobial applications
- Gas scrubbing
- Iron/metals removal
- Filamentous bulking control
- Inorganic toxic pollutant destruction, sulfide oxidation
- Inorganic toxic pollutant destruction, cyanide treatment
- Inorganic toxic pollutant destruction, dechlorination
- Inorganic toxic pollutant destruction, arsenic removal
- Organic toxic pollutant destruction formaldehyde oxidation
- Organic toxic pollutant destruction mercaptan. control (US Peroxide, 2014).

Clearly, the number of applications for hydrogen peroxide is great and the industries that utilize it vary widely.

13.3 Recycling and reuse

The process of manufacturing hydrogen peroxide is a very efficient one in terms of recycling materials that are used. As mentioned, the anthraquinone and the solvents are routinely recycled, as is the metal catalyst.

Since virtually all hydrogen peroxide is used in some reaction to produce other chemicals or user-end products, none of it is recycled.

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14 Lithium

The least dense metal on the periodic table, lithium, has a density of 0.534 g/cm^3, which is even less than that of aluminum (2.699 g/cm^3), another light metal produced on an industrial scale. This property alone makes lithium an extremely useful metal in numerous applications where minimizing total weight is either necessary or desired. Since it can only gain or lose one electron, it is also useful in applications and systems where no over-oxidation can be tolerated.

14.1 Mining and sources

There is one brine operation in the United States, in Nevada, from which lithium is extracted, at Searles Lake. But the figures from this operation are not reported to the United States Geological Survey, to protect proprietary, corporate data (USGS, 2014). The entire world's production, less this Nevada operation, is shown in Figure 14.1 in terms of metric tons. This pie chart does not mention two nations, Bolivia and Afghanistan, which have or are estimated to have enormous reserves of lithium minerals.

In the case of Bolivia, large-scale mining and production of lithium in the Uyuni salt flats area has only just begun. There is no infrastructure in Bolivia at present that can rapidly move to extraction of lithium salts and minerals on a large scale; and thus the Bolivian government is negotiating with other firms and foreign governments for rights to extract and export lithium materials.

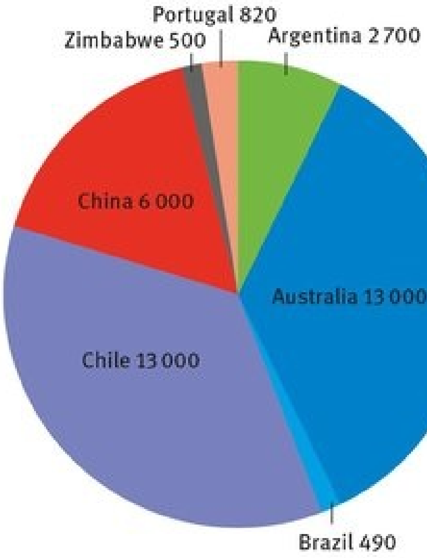
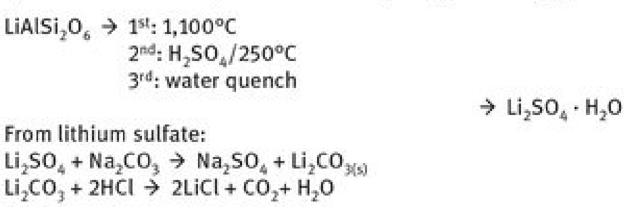


Fig.14.1: Worldwide lithium sources USGS (2014).

In the case of Afghanistan, an official Soviet document outlining possible reserves of numerous minerals including lithium apparently resurfaced after the United States military intervention in the country (Minerals In Afghanistan, 2014). But no mining company or concern has yet begun any extraction of spodumene or any other lithium-bearing minerals or salts.

14.2 Extraction chemistry

There are several lithium ores, as well as large deposits of what is best called lithium brine in certain parts of the world. Spodumene, a lithium aluminum silicate, is one ore that is refined into useable lithium salts. The chemistry can be represented as shown in Figure 14.2.



Spodumene can be represented as $LiAl(SiO_3)_2$ or $LiAlSi_2O_6$.

$LiAlSi_2O_6$ → 1st: 1,100°C
2nd: H_2SO_4/250°C
3rd: water quench
→ $Li_2SO_4 \cdot H_2O$

From lithium sulfate:
$Li_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + Li_2CO_{3(s)}$
$Li_2CO_3 + 2HCl \rightarrow 2LiCl + CO_2 + H_2O$

Fig. 14.2: Lithium extraction from ore.

Lithium chloride can then be mixed with potassium chloride in a 55:45 ratio and elec-trolysized at 450°C to reduce the lithium.

$$\mathrm{LiCl{:}KCl} \xrightarrow[\text{elec.}]{} \mathrm{Li}_{(s)}$$

This process seems cumbersome at first, but since there are few lithium salts that occur as simple mineral structures, it is the necessary purification route. Also, production and isolation of lithium carbonate is important when producing many types of lithium-based batteries.

There are estimates and predictions that in the future the isolation of lithium chloride from brines in the countries listed in Figure 14.1 will make the production of lithium salts and lithium metal economically more attractive, but these remain speculative at the present. Figure 14.3 shows the simplified reaction chemistry that produces lithium hydroxide, a valuable commodity.

$$\mathrm{2\,LiCl + Na_2CO_3 \rightarrow 2\,NaCl + Li_2CO_3}$$
then
$$\mathrm{Li_2CO_3 + Ca(OH)_2 \rightarrow LiOH + CaCO_{3(s)}}$$

Fig. 14.3: Lithium hydroxide production.

Table 14.1: Uses of lithium (USGS, 2014).

Area of use	Amount (%)	Comments
Ceramics and glass	30	Li_2CO_3 is used in firing, becoming Li_2O (Digitalfire Ceramic Materials Database, 2014)
Batteries	22	Small, rechargeable, for portable electronics, as well as electric vehicle batteries (Western Lithium, 2014; International Lithium Corporation, 2014)
Lubricating	11	Lithium 12-hydroxystearate, high

greases		melting point
Air treatment	4	“Lithium bromide brine (54%) is used as a stable, chlorofluoro-carbon-free absorption medium.” (Rockwood Lithium, 2014)
Metallurgical	4	Flux
Polymers	3	Alkyl lithium, catalyst or initiator.
Pharmaceuticals	2	Carbon–carbon bond formation
Primary aluminum production	1	
Military fuels	<1	$LiAlH_4$, rocket propellant additive
Other	23	

14.3 Uses

There has been a fair amount of coverage in the general media in the past 5 years about the use of lithium as a battery material, especially about its potential for use as a new generation of batteries for electric automobiles. There are even now Electric Vehicle Associations and networks (Electric vehicle organizations, 2014). But the profile for uses of lithium and lithium salts is somewhat greater than simply this one use. It can be seen in Table 14.1.

14.3.1 Ceramics and glass

As mentioned in Table 14.1, it is lithium carbonate that can be utilized in the production of various ceramics and glasses. The firing process effects the transformation to lithium oxide. However, lithium oxide itself is used as a flux in glass making, since it results in glasses with small coefficients of thermal expansion. This makes the resulting glasses useful in consumer end-use materials such as ovenware, in which the object must be able to withstand repeated heating and cooling cycles.

14.3.2 Lithium batteries

Lithium battery chemistry does not involve reduced lithium metal, but rather utilizes lithium–cobalt salts. Lithium–cobalt oxide is the current mixed metal salt used with graphite in many lithium batteries. The reaction chemistry for the charge and discharge of one type of lithium battery can be shown as seen in Figure 14.4.

$$\begin{array}{ll} LiCoO_2 + C_6 \rightarrow Li_{1-x}CoO_2 + Li_xC_6 & \text{initial charging} \\ Li_{1-x}CoO_2 + Li_xC_6 \rightarrow Li_{1-x+y}CoO_2 + Li_{x-y}C_6 & \text{Discharge} \end{array}$$

Fig. 14.4: Lithium transfer in lithium–cobalt oxide batteries.

The first reaction illustrates the loss of some lithium into the graphite. Since the amount lost is not precise, it is simply designated as “x.” The second reaction shows the discharge, and the return of a somewhat smaller amount of lithium back to the lithium–cobalt salt. Once again, this amount is not known precisely, and thus is designated as “y.”

The $LiCoO_2$ itself must be synthesized at 900 °C, and contains Li^+ and Co^{3+} between planes of O atoms. Lithium–air batteries represent somewhat different reaction chemistry than that shown above, in part because of the different environments in which they can run. For example, in an acidic electrolytic environment, lithium oxidation occurs as shown in Figure 14.5.

$$4\,Li + O_2 + 4\,H^+ \rightarrow 4\,Li^+ + 2\,H_2O$$

Fig. 14.5: Lithium–air battery, acidic reaction.

The subsequent reduction of the oxidized lithium sometimes produces lithium hydroxide. Lithium–air batteries can also function in a basic or alkaline environment, as shown in Figure 14.6.

$$4\,Li + O_2 + 2\,H_2O \rightarrow 4\,LiOH$$

Fig. 14.6: Lithium–air battery, basic reaction.

As shown, water must participate in the reaction when the metal oxidation occurs. In both of the above cases, different cathode materials are being developed to effect the reduction of lithium from its oxidized state (Lithium Air Industries, 2014).

14.3.3 Lubricating greases

There is certainly no overarching theory concerning the production of greases and lubricants. Rather, any specific grease is used simply because it works well in a known, defined application. For example, lithium 12-hydroxystearate is produced on a large scale because it has desirable viscosity, melting point, and other characteristics for several applications. Figure 14.7 shows the Lewis structure of the molecule.

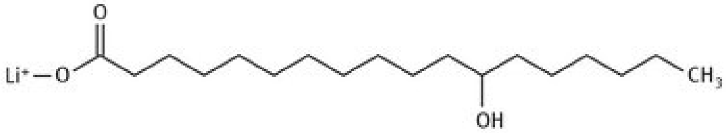


Fig. 14.7: Structure of lithium 12-hydroxystearate.

This stearate is made by adding lithium hydroxide slowly to a heated solution of the hydroxyl-stearic acid. In turn, this fatty acid can be extracted from the triglycerides in castor oil.

14.3.4 Air treatment

Lithium compounds are at times used in heating, ventilation, and air-conditioning systems (HVAC). The reason lithium salts are used in large air treatment operations (the HVAC systems of large commercial buildings, for example) is because of the dessi-cant capabilities of several lithium salts. Given sufficient time, lithium salts, such as lithium chloride, can actually pull enough moisture from air that they solvate entirely, resulting in a brine solution, a laboratory-scale example of which is shown in

Figure 14.8. This broken container of one pound of lithium chloride was simply stored in the beaker, as shown, for slightly more than 1 year. It was originally a white powder and eventually became a brine solution. The lithium chloride brine level is noted, as is a break in the jar.

Perhaps obviously, in commercial building HVAC systems, lithium salts scavenge moisture, but must then be able to release it to an exhaust vent, in the process redrying the lithium salt.

Fig. 14.8: Broken container of lithium chloride after 1 year.

14.4 Potential uses

The lithium battery technology outlined above, as well as several other lithium-containing materials, has already been proved to be effective as batteries in small electronic devices and in much larger batteries used in battery-powered vehicles (automobiles and light trucks). However, whether such processes will be scaled up to meet the demands of the developed world for automotive transport remains in question. Current internal combustion engines and gas tanks generally enable a trip of 300 miles without refueling, acceleration from 0–60 miles per hour (0–100 kph) in less than 15 s, and refueling stops that last less than 10 min. These specifications will have to be met for any electric vehicle to be commercially successful, simply because consumers are now accustomed to these standards and do not wish to compromise them. Currently, electric vehicles do not have this range, recharging times are significantly longer than 10 min, and there is no infrastructure for “recharging stations” throughout the country as there is for gas stations. Should these technical hurdles be overcome though, the potential for electric vehicles to claim a large share of the automotive market is great, and has the potential to change the world’s economy.

14.5 Recycling

Since lithium has such a broad profile of applications and uses, and since some of it includes very small consumer end-use devices, it is difficult to think that all of it can be recycled. Lithium batteries however can definitely be recycled. At the moment, small lithium batteries in portable electronics are not necessarily recyclable, simply because the cost of doing so is too high based on the size of the unit – meaning each battery is very small. But the companies that are marketing automobiles powered by lithium batteries have plans for large-scale recycling operations as the cars and the batteries reach the end of their useful life, or have plans for a second use of the batteries asas connected, stationary, and large power storage units.

As the recycling of large lithium batteries becomes established, a great deal of political interest in such processes may develop, since criticism has already been voiced that a total shift from gasoline-powered automobiles to battery powered automobiles may simply equate to a shift from dependence on Middle-East oil to a dependence on South American lithium. What makes this unpalatable to many users and political policy makers is that the governments in both areas do not necessarily have agendas and human rights records that are in harmony with the countries in which the end products – gasoline or lithium batteries – are largely being used.

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15 Tungsten

Tungsten is one of the only handful of elements on the periodic table that has a symbol not derived from a Latin or Greek root word, and a name not derived from either. The symbol, “W” comes from the German word “wolfram,” and the word “tungsten” comes from the Swedish for “heavy stone.” The term “wolfram” in turn comes from the name of the ore wolframite, which apparently comes from old German “Wolf Rahm” meaning “wolf cream.” This rather odd term, in turn, appears to be related to the fact that significant amounts of another metal must be oxidized during the reduction and isolation of tungsten (perhaps turning the other metal into a white oxide).

Since its discovery and isolation in 1783, tungsten has found numerous uses in materials and alloys that require hardness, abrasion resistance, and durability. It remains desirable for these properties today, is tracked by the USGS Minerals Commodity Summaries annually (USGS, 2014), and remains of interest to the world’s militaries and construction industries.

15.1 Mining and sources

There is one tungsten mine in the United States, but the USGS does not report its output, citing company proprietary data. Ignoring this, the world production of tungsten is shown in Figure 15.1, in terms of metric tons. Although now China dominates the world market, simply because of the size of its reserves, the demand for the tungsten mined in Portugal was high immediately before and during the Second World War.

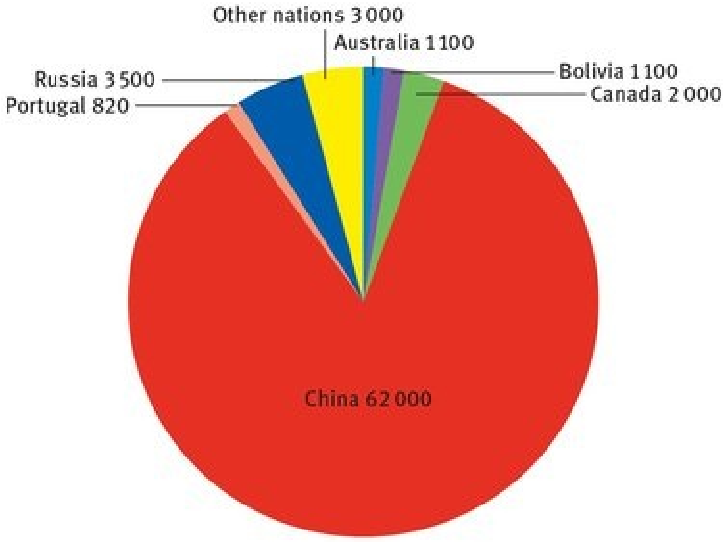

Fig. 15.1: World tungsten production.

This is because China was partially occupied by the armed forces of the Empire of Japan at the time, and Portugal was neutral, and was willing to negotiate with both Allied and Axis nations.

The number of companies and firms that deal with tungsten, from refining, to product development, to sales, is huge. The International Tungsten Industry Association posts a lengthy list of its members on its website (International Tungsten Association, 2013), several of whom also deal with other metals. Additionally, the pie chart does not take into account the amount of tungsten-bearing material that is recycled worldwide. Because of the expense involved in its extraction and purification, this makes up a significant portion of tungsten used each year.

15.2 Extraction chemistry

Tungsten is only found in ores in nature, and not in its reduced form. The minerals wolframite and scheelite are the principle ores from which it is extracted. Table 15.1 gives information on tungsten ores.

The extraction of tungsten involves oxidizing the tungsten in the ores to the +6 state, making it into WO_3, and ridding it of impurities. From that point, the material can be reduced. A simplified chemistry is as follows in Figure 15.2.

$$WO_3 + 3\,H_{2(g)} \rightarrow W_{(s)} + 3\,H_2O$$

or

$$2\,WO_3 + 3\,C \rightarrow 2\,W_{(s)} + 3\,CO_2$$

Fig. 15.2: Isolation of tungsten.

Interestingly, scheelite crystals can be made synthetically by what is called the Czochralski process, a process which is more commonly used to make high-purity silicon and semiconductor materials. A melt of the material has a seed crystal introduced, and the seed is slowly drawn from the molten sample. As the cooling material is elevated and drawn, a crystal grows. In the case of scheelite, this is done to produce gem quality stones. In the past, these synthetic gemstones have sometimes been used to simulate diamonds.

Table 15.1: Tungsten ores.

Ore	General formula	Comments
Ferberite	$FeWO_4$	Iron-rich variant of wolframite
Huebernite	$MnWO_4$	Manganese-rich variant of wolframite
Scheelite	$CaWO_4$	Major source of W
Wolframite	$(FeMn)WO_4$	Major source of W

Table 15.2: Uses for tungsten (International Tungsten Association, 2013).

Item	Application	Comments
Cemented carbide parts	Wear-resistant and cutting materials	Usually as tungsten carbide, WC or W_2C, with

		a m.p. =2770°C.
Heavy alloys	High-density materials	Up to 18% W in the alloy. Alloyed with Co, Fe, Ni.
Electronic components	Wires, filaments, electrodes	Used for corrosion resistance.
Steels	Superalloys, wear-resistant alloys	Hastelloy and stellite, for turbine blades.
Chemicals	WO_x ceramic glaze	
	WS_2 lubricant	Can withstand elevated temperatures.
	WO_3 catalyst	

15.3 Uses

The profile for the use of tungsten-based materials is broad, but is dominated by the production of cemented carbide parts. A more complete listing is shown in Table 15.2.

The general public often thinks of light bulb filaments as the primary end use product for tungsten metal in a reduced form, but there are uses beyond this for the metal. It is also used in other applications where filaments are required, as well as in what is called tungsten inert gas welding (TIG welding).

15.4 Recycling and reuse

Tungsten is a metal that is recycled from numerous end-use products. The USGS states, “In 2012, the tungsten contained in scrap consumed by processors and end users represented approximately 52% of apparent consumption of tungsten in all forms” (USGS, 2014).

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16 Sodium

Over the past 50 years, reduced sodium metal has become a large commodity material and an economically useful one. Prior to this, while small amounts of the metal were produced, sodium existed and was being used in its oxidized form, usually as common table salt, although salts such as sodium hydroxide were known and utilized. Common salt has an ancient history and myriad uses, but here we will only discuss the production and use of sodium metal.

16.1 Sources

Sodium occurs in the Earth and oceans as sodium chloride. While there are other sodium-containing salts and minerals, sodium chloride is by far the the most abundant, and is either mined or evaporated from briny water, and then either used as is or reacted chemically to produce other materials, one of them being the sodium metal.

Salt is so common throughout the world that while the USGS Mineral Commodity Summaries tracks it each year and a Salt Institute is devoted to promoting its many uses (USGS, 2014; Salt Institute, 2014), as well as those of soda ash and sodium carbonate, there appears to be no fear that sodium chloride will ever be depleted.

16.2 Extraction chemistry

The electrolysis of salt water does not produce sodium metal. Rather, it produces sodium hydroxide, hydrogen gas, and chlorine gas. The reaction chemistry is fairly simple, and is

$$2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + Cl_{2(g)} + H_{2(g)}$$

This is indeed a major industrial process, the chlor-alkali process, in which all three products are used.

The current industrial process by which sodium metal is isolated is an electrolysis of molten sodium chloride. This is a smaller process globally than many of the others we have examined, but still produces approximately 100,000 tons of the metal each year. The process occurs in a refractory chamber, called a Downs cell. The scheme is shown in Figure 16.1. The reaction chemistry for the Downs cell is deceptively simple, as shown:

$$2NaCl_{(l)} \longrightarrow 2Na_{(l)} + Cl_{2(g)}$$

What the reaction does not show is the energy input needed to make this reaction occur. The cell is normally kept at approximately 600 °C, and even at that temperature the starting material must be a mixture of sodium chloride and calcium chloride.

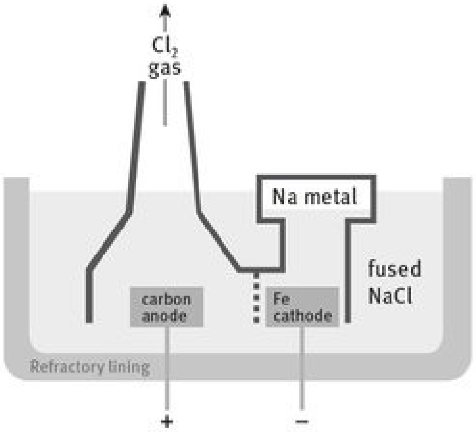

Fig. 16.1: Downs cell.

Without the latter, the temperature would have to be even higher. However, calcium chloride is so different in electronegativity that only sodium is reduced from the mixture. Both products are less dense than the molten mixture, and thus rise to the top, as shown in Figure 16.1.

The Castner process is older and somewhat more expensive than the use of Downs cells for sodium production, and thus has been replaced. But it represents a different way to produce sodium metal, starting with sodium hydroxide. It too is an electrolysis. The reaction chemistry runs at 330 °C and can be represented as

$$2NaOH_{(l)} \longrightarrow 2Na_{(l)} + \tfrac{1}{2}O_2 + H_2O$$

While the production of water, listed on the same side of the reaction as the sodium product, seems impossible, the water is dissolved in the molten electrolyte and thus does not ignite the reduced metal. However, build-up of small amounts of water does decrease the yield of the product.

The Deville process has also been entirely replaced by the use of Downs cells, but it does represent the earliest large-scale isolation of sodium. Sodium carbonate is the starting material instead of sodium chloride, and the reaction chemistry can be expressed as follows:

$$2C + Na_2CO_3 \longrightarrow 2Na + 3CO$$

In the reaction, carbon is used as the reducing agent, and the entire reaction takes place at approximately 1100°C.

16.3 Uses

Uses of sodium metal, or for it as a starting material for further chemicals, are listed in Table 16.1. Major uses are listed here, as the profile becomes rather wide when all the small or niche uses are considered.

Table 16.1: Uses for sodium.

Material	Use	Comments
Sodium	Heat transfer	Used in nuclear reactors, has

Sodium metal	Heat transfer fluid	Used in nuclear reactors, has high thermal conductivity
Sodium metal	Vapor lamps	Used in street lighting
Sodium fusion test		An older qualitative test for nitrogen, sulfur, and halogens in organic compounds.
Alloys		NaK alloys are used as oxygen scavengers
Sodium amide	Indigo dye	Used in Pfleger’s synthetic method
Sodium azide	Automotive airbags	Wislicenus process: $2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2$ Then $2NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$
Sodium borohydride	Pulp industry, dyeing industry	Made via: $4NaH + B(OCH_3)_3 \rightarrow 3NaOCH_3 + NaBH_4$
Sodium hydride	Production of sodium borohydride	Formed by direct addition: $2Na + H_2 \rightarrow 2NaH$
Tri-phenyl phosphine	Organic syntheses	$6Na + PCl_3 + 3PhCl \rightarrow PPh_3 + 6NaCl$

16.4 Other, heavy alkali metal production and uses

Of the other alkali metals, only potassium is present and reachable in the Earth’s crust in large enough quantities to be mined and extracted. Potash (potassium hydroxide, KOH) is by far the most common potassium-containing mineral, although there are several more. When pure potassium is needed, it can be separated from potassium chloride by what is called the thermal method, using sodium, as shown here:

$$KCl + Na \longrightarrow NaCl + K$$

It can also be separated from its fluoride by what is called the Griesheimer process, which utilizes calcium carbide, as shown here:

$$CaC_2 + 2KF \longrightarrow 2K + CaF_2 + 2C$$

Industrially, potassium is used almost exclusively as one of the potassium salts. These account for its use in fertilizer, gunpowder, and numerous other applications. The production of potassium metal is a much smaller scale operation than the production of sodium metal.

16.5 Recycling

As with many of the materials discussed in this book, sodium is so often used in producing other materials that there is no recycling of any of it.it.

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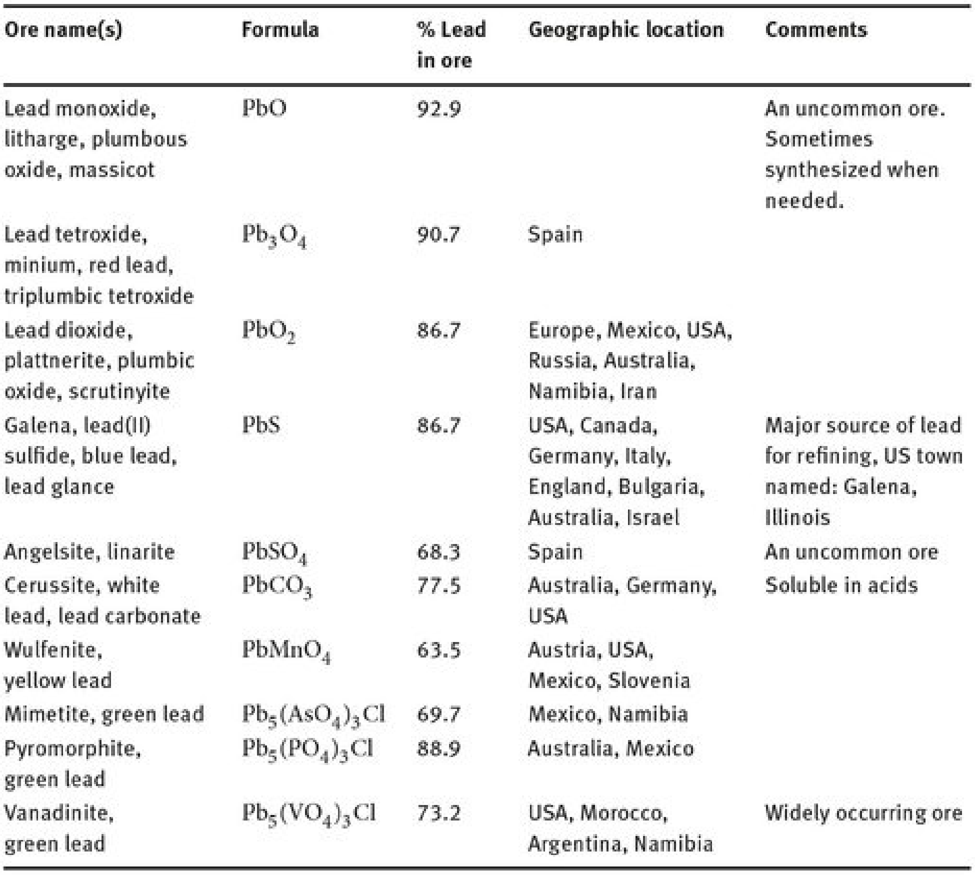
17 Lead

Lead metal is one of only a few metals known to have been used in ancient times. The atomic symbol for it, Pb, derives from the Latin word, plumbum. The English word plumber is also derived from this word, since metal plumbing and materials to direct water were historically often made from lead.

17.1 Sources

Lead is rarely found in its reduced state in nature. Rather, several oxide and sulfide ores exist, all of which contain varying amounts of lead. Ores – often mixed ores –with as little as 5% of the element can generally be refined, so that the lead can be reduced and used. Table 17.1 shows the major types of lead ores.

Table 17.1: Sources of lead (Handbook of Mineralogy, 2014).



Ore name(s)	Formula	% Lead in ore	Geographic location	Comments
Lead monoxide, litharge, plumbous oxide, massicot	PbO	92.9		An uncommon ore. Sometimes synthesized when needed.
Lead tetroxide, minium, red lead, triplumbic tetroxide	Pb_3O_4	90.7	Spain	
Lead dioxide, plattnerite, plumbic oxide, scrutinyite	PbO_2	86.7	Europe, Mexico, USA, Russia, Australia, Namibia, Iran	
Galena, lead(II) sulfide, blue lead, lead glance	PbS	86.7	USA, Canada, Germany, Italy, England, Bulgaria, Australia, Israel	Major source of lead for refining, US town named: Galena, Illinois
Angelsite, linarite	$PbSO_4$	68.3	Spain	An uncommon ore
Cerussite, white lead, lead carbonate	$PbCO_3$	77.5	Australia, Germany, USA	Soluble in acids
Wulfenite, yellow lead	$PbMnO_4$	63.5	Austria, USA, Mexico, Slovenia	
Mimetite, green lead	$Pb_5(AsO_4)_3Cl$	69.7	Mexico, Namibia	
Pyromorphite, green lead	$Pb_5(PO_4)_3Cl$	88.9	Australia, Mexico	
Vanadinite, green lead	$Pb_5(VO_4)_3Cl$	73.2	USA, Morocco, Argentina, Namibia	Widely occurring ore

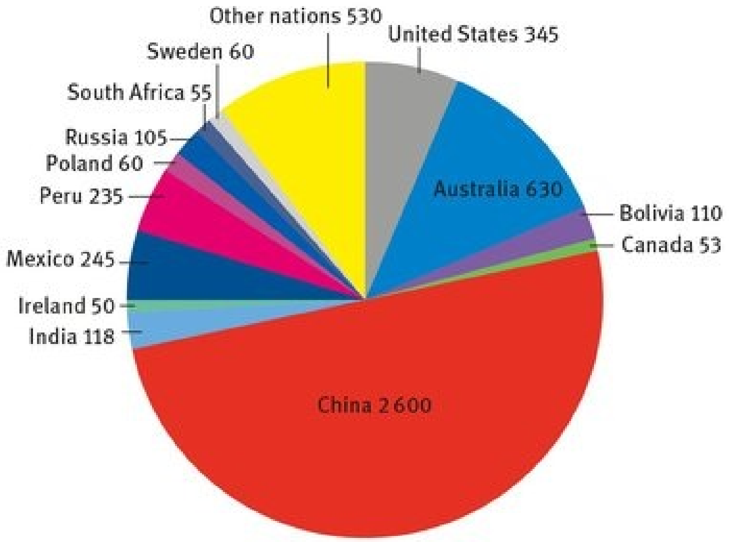


Fig. 17.1: Global lead production (USGS, 2013).

The United States Geologic Survey (USGS) does track lead production in its Mineral Commodity Summaries each year (USGS, 2013). A global breakdown of lead production is shown in Figure 17.1, in terms of thousands of metric tons. This figure does not take into account recycled lead metal, only that which has been refined from ores.

17.2 Extraction chemistry

The extraction of lead from lead ores is not always easy to represent with simple chemical reactions, because lead ores occur with lead co-mingled with several other metal elements, often metals such as silver. In such cases, lead is considered the co-product of silver, with silver being the more expensive metal.

One example of this co-production is the lead (and silver) of Bolivia. The famous Potosi mines, which fueled the royal coffers of Spain with silver from the 1500s until the waning of Spain's New World empire in the 1800s, produced enough silver metal that South American silver had displaced European silver in European coinage by the 1580s. The mines still function today long after Bolivia's independence, but now lead is the primary metal that is extracted, and silver the secondary.

Lead is separated from silver by what is called the Parkes process. The process utilizes molten lead that contains silver as impurities. Zinc is added to the melt, because it is not miscible with lead, but does become a molten alloy with the silver. The reaction chemistry can be simplified to the following:

$$\mathrm{Pb{:}Ag_{(l)} + Zn_{(s)} \longrightarrow Zn{:}Ag_{(l)} + Pb_{(l)}}$$

The zinc–silver alloy forms a separate layer from the lead, and is separated from it, leaving a pure lead behind. The zinc–silver alloy is then heated, vaporizing the zinc. The reaction chemistry for this can be presented as follows:

$$\mathrm{Zn{:}Ag_{(l)} \longrightarrow heat \longrightarrow Ag + Zn_{(g)}}$$

The process works well because zinc and lead are essentially immiscible and because zinc is quite inexpensive. This process also works to remove gold as an impurity in a predominantly lead product. This was patented (number 13,118) by Alexander Parkes in 1850, and thus is a very mature chemical technique that is still used today.

17.3 Uses

The general public thinks of automotive batteries as the main use of lead metal, but there are several others as well (USGS, 2013; EUROBAT, 2014; Battery Council International, 2014). They include: ballast, diving weights, counterweights, and radiation shielding materials. The US Department of Defense Strategic and Critical Materials 2013 Report on Stockpile Requirements list major uses of lead as: “storage batteries, ammunition, broadcast and wireless communications equipment” (US Department of Defense Strategic and Critical Materials, 2013).

Leaded glass

What is often referred to as lead glass generally contains between 20% and 40% lead oxide (PbO) in the final material. Calcium is often present in glass, and is replaced by the lead oxide to make this product. The process of making this type of glass is over 300 years old, and has been used over that time with only minor modifications. The clarity of the finished glass makes it desirable for many products, and the lead oxide added to it actually makes it easier to melt and less energy intensive to form.

17.4 Recycling

Lead metal recycling is a mature industry, with the lead from lead-acid batteries being recycled worldwide (America’s Battery

Recyclers, 2014). The sulfuric acid used in such batteries is so inexpensive that the vast majority of it is neutralized and discarded, but the plastic housing and the lead metal are routinely recycled.

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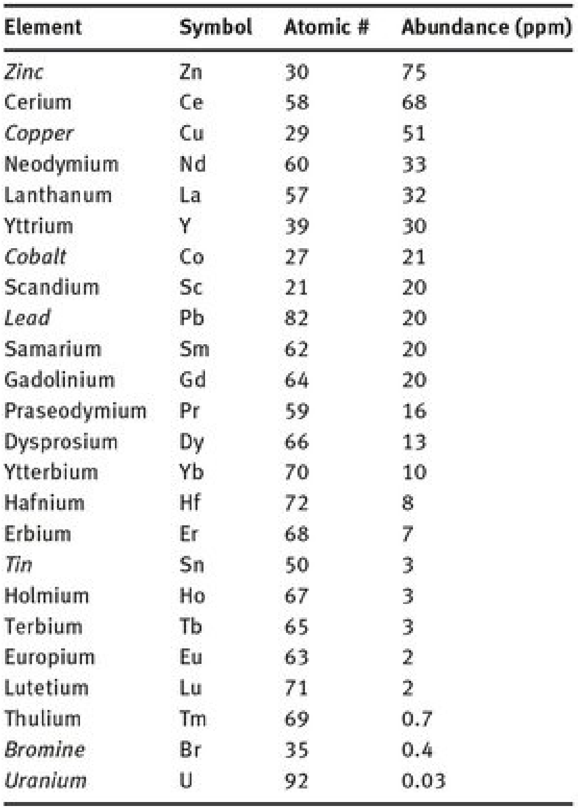
18 Rare earth elements

We will use the older term “rare earth” here to describe and encompass all the lanthanide elements as well as yttrium and scandium. This general definition is that used by the International Union of Pure and Applied Chemistry (IUPAC), with the latter two elements included with the lanthanides because of their co-occurrence in many lanthanide-bearing ores. These elements are also called the lanthanides, the lanthanoids, and the inner transition metals, depending upon the publication that is discussing them.

Despite this older name, the rare earth elements are not particularly rare; rather, they are not concentrated in small areas where a mining operation is able to extract just one from a specific location. Their relative abundance in the Earth’s crust, in relation to several other elements, is shown in Table 18.1. It can be seen that some elements that find industrial scale uses are actually believed to be present in the Earth’s crust in lower abundances than many of the rare earth elements. Examples include bromine and uranium, shown at the bottom of Table 18.1. Even tin is less common than several of the rare earth elements.

Table 18.1: Abundance of the rare earth elements.



Element	Symbol	Atomic #	Abundance (ppm)
Zinc	Zn	30	75
Cerium	Ce	58	68
Copper	Cu	29	51
Neodymium	Nd	60	33
Lanthanum	La	57	32
Yttrium	Y	39	30
Cobalt	Co	27	21
Scandium	Sc	21	20
Lead	Pb	82	20
Samarium	Sm	62	20
Gadolinium	Gd	64	20
Praseodymium	Pr	59	16
Dysprosium	Dy	66	13
Ytterbium	Yb	70	10
Hafnium	Hf	72	8
Erbium	Er	68	7
Tin	Sn	50	3
Holmium	Ho	67	3
Terbium	Tb	65	3
Europium	Eu	63	2
Lutetium	Lu	71	2
Thulium	Tm	69	0.7
Bromine	Br	35	0.4
Uranium	U	92	0.03

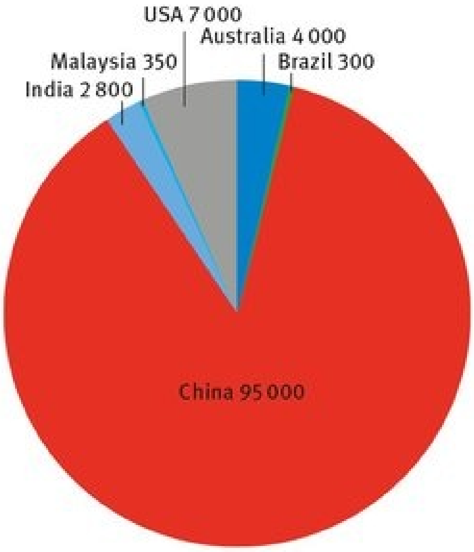


Fig. 18.1: Rare earth element producers (in metric tons of rare earth oxides).

18.1 Sources

While the United States has areas in the Western states from which rare earth elements can be extracted profitably, these have not been utilized in recent years. Rather, rare earth elements have been imported, mostly from China, in large part because such imports are less expensive. The worldwide producers of rare earth metals are shown in Figure 18.1 (US Geological Survey, 2013; RARE, 2014).

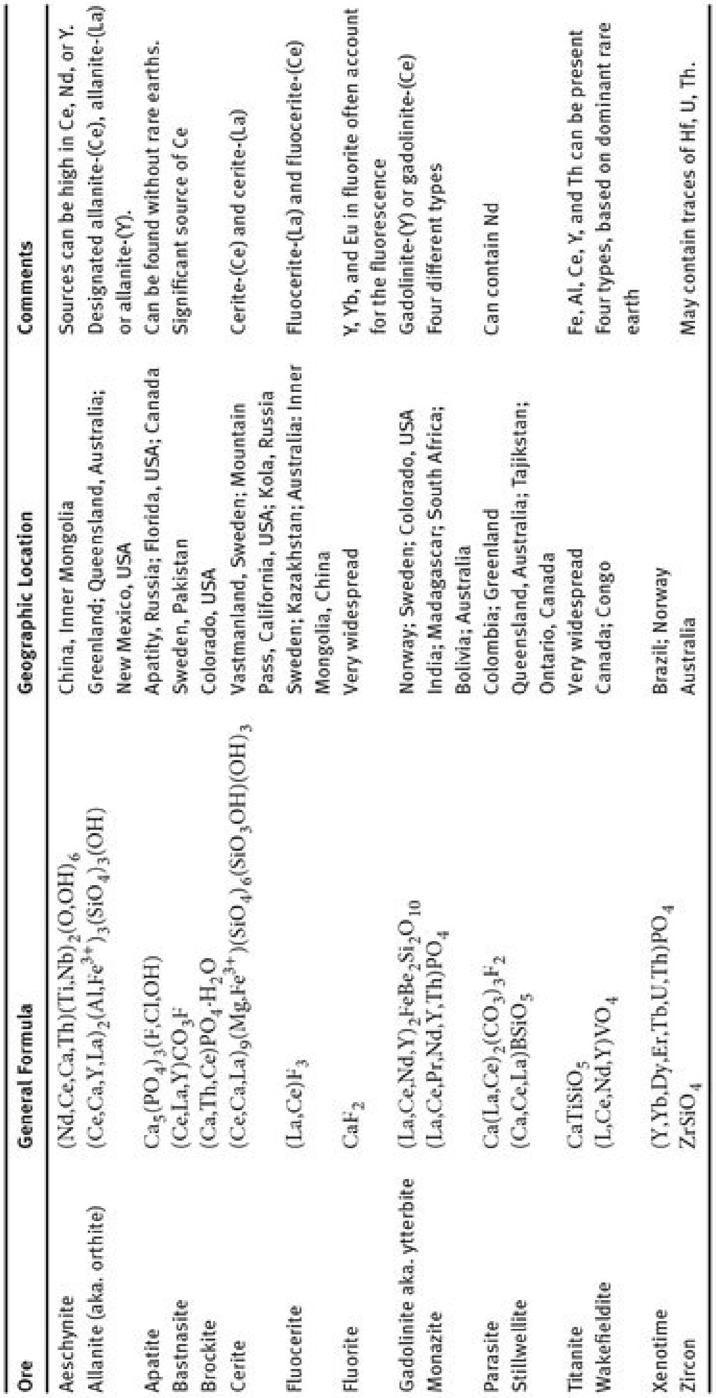
18.2 Extraction chemistry

The extraction chemistry for the rare earth elements remains a challenge, because the reactivity of each element within this set is very close to that of the others, especially those immediately adjacent to it (Holleman and Wiberg, 1995). This is obvious when one looks at the ores from which these elements are refined. The most common ores are generally monazite, bastnasite, and xenotime, but there are several others. Table 18.2 shows the ores containing rare earth elements, and what are their general compositions. The complexity of several of the ores is obvious by their formulae. This also contributes to the difficulty of extracting specific elements from the various ores. But even simple ores, such as fluorite, can contain significant amounts of one rare earth element or another.

18.2.1 Separation and isolation

As mentioned, the separation of individual lanthanides from complex ore mixtures is still a challenge. The ionic radii of these elements are all very close to each other, but methods have been developed for their extraction and isolation. It is not possible to show simple reaction chemistry that illustrates the separation and isolation of each element because there are few cases when all of the lanthanides are present in a single ore sample. Rather, these complex separations are best explained in terms of a list of procedures, as follows:

Table 18.2: Ores containing rare earth elements.



Ore	General Formula	Geographic Location	Comments
Aeschynite	$(Nd,Ce,Ca,Th)(Ti,Nb)_2(O,OH)_6$	China, Inner Mongolia	Sources can be high in Ce, Nd, or Y.
Allanite (aka. orthite)	$(Ce,Ca,Y,La)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$	Greenland; Queensland, Australia; New Mexico, USA	Designated allanite-(Ce), allanite-(La) or allanite-(Y).
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	Apatity, Russia; Florida, USA; Canada	Can be found without rare earths.
Bastnasite	$(Ce,La,Y)CO_3F$	Sweden, Pakistan	Significant source of Ce
Brockite	$(Ca,Th,Ce)PO_4{\cdot}H_2O$	Colorado, USA	
Cerite	$(Ce,Ca,La)_9(Mg,Fe^{3+})(SiO_4)_6(SiO_3OH)(OH)_3$	Vastmanland, Sweden; Mountain Pass, California, USA; Kola, Russia	Cerite-(Ce) and cerite-(La)
Fluocerite	$(La,Ce)F_3$	Sweden; Kazakhstan; Australia: Inner Mongolia, China	Fluocerite-(La) and fluocerite-(Ce)
Fluorite	CaF_2	Very widespread	Y, Yb, and Eu in fluorite often account for the fluorescence
Gadolinite aka. ytterbite	$(La,Ce,Nd,Y)_2FeBe_2Si_2O_{10}$	Norway; Sweden; Colorado, USA	Gadolinite-(Y) or gadolinite-(Ce)
Monazite	$(La,Ce,Pr,Nd,Y,Th)PO_4$	India; Madagascar; South Africa; Bolivia; Australia	Four different types
Parasite	$Ca(La,Ce)_2(CO_3)_3F_2$	Colombia; Greenland	Can contain Nd
Stillwellite	$(Ca,Ce,La)BSiO_5$	Queensland, Australia; Tajikstan; Ontario, Canada	
Titanite	$CaTiSiO_5$	Very widespread	Fe, Al, Ce, Y, and Th can be present
Wakefieldite	$(L,Ce,Nd,Y)VO_4$	Canada; Congo	Four types, based on dominant rare earth
Xenotime	$(Y,Yb,Dy,Er,Tb,U,Th)PO_4$	Brazil; Norway	
Zircon	$ZrSiO_4$	Australia	May contain traces of Hf, U, Th.

1. *Milling*. As with many separation processes for various ores, the first step in this form of extraction is to bring all the material down to a uniform size. This is a mechanical process that crushes larger pieces of any rare earth-containing ore to smaller sizes, with a large

surface area. Through crushing and sieving, the ore can be reduced in particle size to that of rough sands.

2. *Division by electromagnetic means*. A conveyor belt system is used to separate the magnetic substances in any ore from the nonmagnetic ones. This is accomplished by having electromagnets attached to one of the end rollers about which the belt spins. As material drops off the end of the belt to receiver bins, that which is nonmagnetic simply drops, while the magnetic material is attracted to the magnets on the rotary wheel at the end of the belt. This material only drops away when the belt pulls it far enough away from the magnets, as seen in Figure 18.2.

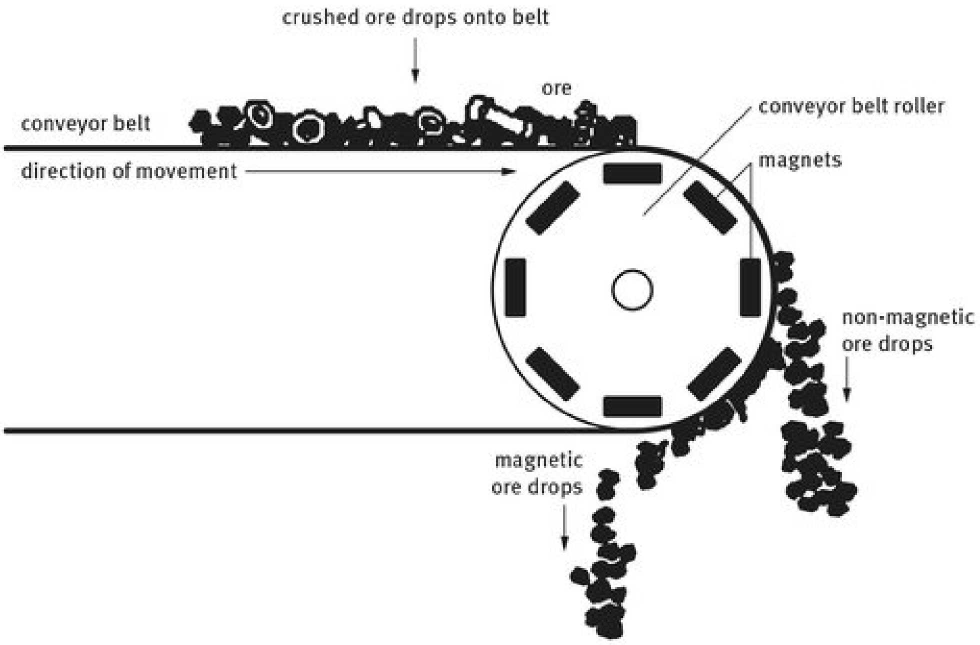


Fig. 18.2: Magnetic ore separation from nonmagnetic ore.

3. *Flotation*. As with the separation of many ores, flotation is a further separation technique based on the density of the batch of ore. The ore is reduced to powder and put into an aqueous solution, usually one that has some surfactant material in the solution as well. Air is blown into the solution, which can separate the finer particles that do not sink.

4. *Centrifugal concentration*. By spinning the remaining material at high speedsinin especially designed centrifuges, the ore can be further separated by the density of the different materials within the batch.
5. *Leaching and precipitation*. The concentrated material can now be separated either as oxides or in some cases as metals, using the following techniques:
    - (a) *Fractional crystallization*. This technique depends on the solubility differences of the various rare earth element salts in the solution. By adjusting temperature and pH carefully, selective precipitation occurs.
    - (b) *Ion exchange*. As the name implies, this technique binds rare earth element ions to some medium, often a synthetic plastic resin or a synthetic zeolite, and solvates other ions into the solution. The rare earth-bearing materials are then washed and treated with acid to isolate the desired products from any other ionic materials remaining in the solution.
    - (c) *Extraction via solvents*. The lanthanides, as soluble salts such as nitrates, are extracted from an aqueous solution into an organic one, such as kerosene, which has a chelating agent in it. One such chelating agent that has seen extensive use is tri-n-butylphosphate. This forms stronger complexes with the rare earth elements that have smaller ionic radii, making those more soluble in the organic phase.
6. *Electrolysis*. Electrolytic deposition of metals can occur if the metal salts are soluble, and if an anodic material can be made soluble during the reduction of the desired rare earth element.

   It should be emphasized that each of these steps may sometimes need to be performed numerous times to achieve complete separation of one of the rare earth elements from another. In some cases, depending upon the batch of ore, a step may need to be performed hundreds of times to concentrate one element and deplete another from a particular solution or precipitate.

18.2.2 Refining to pure rare earth elements

While all of the rare earth elements can be reduced to their metal states, many applications of them do not require this. Table 18.3 gives a brief list of most of the major uses of rare earth elements. It becomes apparent that many of them are used as oxides or some other compound.

Table 18.3: Uses of the rare earth elements.

Name	Use	Form
Scandium	Aerospace metal alloys	Sc−Al alloy
Yttrium	Ceramics, phosphors, alloys	$EuYVO_4$ for phosphors
Lanthanum	Batteries, catalysts for petroleum refining	NiMH battery component
	Glass	$AsLaF_3$
Cerium	Catalysts, auto	Ce_2O_3
	Oven cleaning catalyst	Ce_2O_3
	Optical polishing	CeO_2
	Ceramics	CeO_2
	Optician’s rouge	CeO_2
	Gas mantles	CeO_2

	Alloys	Ce metal
Praseodymium	Magnet alloys	Pr−Nd metal
	Carbon arc lights	$(La)F_x$
	Glass	Mixed
	Fiber optic amplifier	Mixed
	Mischmetal	Pr, Ce, La, Nd
Neodymium	Magnets	NdFeB alloy
Promethium	Beta radiation emitter	As oxide or chloride
Samarium	Magnets	Sm−Co alloy
	Reactor control rods	Alloy component
Europium	Liquid crystal displays	Eu_2O_3
Gadolinium	Numerous niche uses	Usually as alloy component, or as oxide
Terbium	Phosphors	$Tb:Gd_2O_2S$
	Magnets	Minor component
Dysprosium	Magnets	Nd−Fe−B−Dy, up to 5% Dy
	Lasers	Dy−V
Holmium	High power magnets	As alloy
Erbium	Lasers	$Y_3Al_5O_{12}$: Er
	Specialty glasses	As a dopant
Thulium	X-ray device source	As reduced metal
	Lasers	$Tm:Ho:Cr:Y_3Al_5O_{12}$
Ytterbium	Stainless steel	Minor dopant
	Fiber optics	As dopant

	Fiber optics	As dopant
Lutetium		Few commercial uses

18.3 Uses

The profile of uses for the rare earth elements is almost as wide and varied as the composition of the ores from which they are refined. Perhaps the most obvious recent use of any of the rare earth elements is as a component of the small magnets that are incorporated into cellular phones. Without the use of such magnets, cell phones would conceivably still be available in the size of the portable phones first commercialized in the 1980s. Table 18.3 shows common uses for each lanthanide. Many are niche uses.

It can be seen from Table 18.3 that several of these elements find use in high strength magnets, as well as in various types of lasers. Indeed, such products continue to be used in more niche applications each year, prompting warnings from the United States Department of Energy Ames Research Lab about the perceived loss of technical ability in this area within the United States. Leading expert Dr Karl Gschneider is particularly keen on ensuring that future scientists are trained in the use and refining of rare earth elements, and able to make advances in such fields (US Department of Energy, 2014).

18.4 Recycling

The recycling of rare earth elements is still in its infancy, although some commercial efforts have been made in Japan (Japan Recycles Minerals, 2010). One of the difficulties in large-scale recycling of rare earth elements is simply removing them from the user end products in which they reside in some economically feasible manner. This is because the amount used per unit is usually quite small, such as the magnet material in a cell phone. Some efforts at recycling items such as cell phones are already underway, though. Figure 18.3 shows one such recycling kiosk in a shopping mall near Detroit, Michigan, USA.

Fig. 18.3: Automated cell phone recycling kiosk.

As with most recycling programs, the incentive is economic rather than one of scarcity of the materials. In general, it is believed that there is more than a century of rare earth elements left that can be extracted from ores. But recycling may prove to be less expensive.

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19 Thorium

Thorium is one of only a few naturally radioactive elements that has a colossally long half-life, over 14 billion years. Despite its natural radioactivity, thorium has yet to be used as fuel in a commercially functional nuclear power plant, instead of being used in several small, niche applications.

Several countries have exerted some efforts in the direction of thorium-based nuclear power, mostly because a large amount of thorium is available, and because it is extremely hard to convert any products from spent thorium fuel into a weapons-grade fissile material. India may be the first country to harness thorium to this purpose, in large part because India has large deposits of thorium-containing minerals (USGS, 2013; The International Thorium Energy Organization, 2014).

19.1 Sources

Monazite is a mineral that can not only be considered a major source of the element thorium, but it also always contains some lanthanide elements. Because thorium is not used in large quantities compared to many other industrially important metallic elements, the United States Geologic Survey tracks it in terms of reserves of thorium oxide (ThO_2), and does not list refinery production (USGS, 2013). This thorium oxide, or thoria, production is often a secondary product with rare earth elements being the primary product.

Figure 19.1 shows the current world thorium reserves of different countries, measured in terms of metric tons of ThO_2. One can see that the total world reserve is only 1.4 million tons, which is much less than several other industrially useful metals.

A word of caution is in order when discussing thorium reserves: these estimates may change significantly in coming years. Currently, there is not a high demand for thorium. Should thorium-based nuclear reactors become an important way to produce electricity in coming decades, there will be much more intense exploration for monazite and thus for thorium deposits (The International Thorium Energy Organization, 2014; Martin and Richard, 2013; Greentech Media, 2014).

19.2 Extraction chemistry

The extraction processes for thorium are relatively complex because thorium always occurs in conjunction with several of the lanthanide elements. As mentioned, monazite is the mineral from which thorium is generally refined although thorite contains more thorium by the mass percentage of mineral. But monazite is also a mineral from which several rare earth elements are refined, as discussed in Chapter 18. Usually, refining of the rare earth elements is the economic driving force for the extraction of materials from monazite. The United States Geological Survey Mineral Commodity Summaries 2013 states:

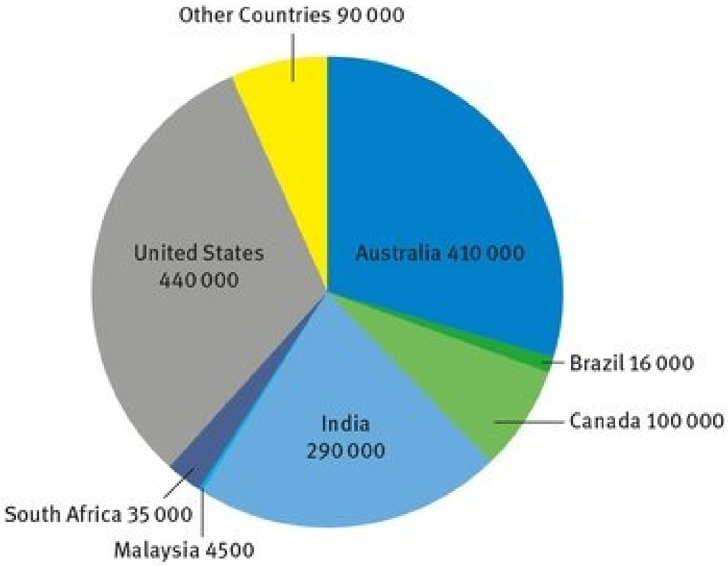


Fig. 19.1: World thorium reserves.

Reserves are contained primarily in the rare-earth

> ore mineral monazite and the thorium mineral thorite. Without demand for the rare earths, monazite would probably not be recovered for its thorium content. Other ore materials with higher thorium contents, such as thorite, would be more likely sources if demand significantly increased (USGS, 2013).

A very simplified chemistry for the isolation of thorium from a lanthanide-containing ore is shown in Figure 19.2.

$$\mathrm{LnO}_x + \mathrm{H_2SO_4} \rightarrow \mathrm{LnSO}_{4(aq)}$$

$$\mathrm{LnSO}_{4(aq)} + \mathrm{NaOH} \rightarrow \mathrm{Th(OH)}_{4(s)} + \mathrm{LnSO}_{4(aq)}$$

Fig. 19.2: Thorium isolation.

In the first equation, Ln represents the mix of lanthanide elements and thorium, and the reaction must be heated to produce a solution of lanthanide–thorium sulfates. In the second reaction, the reaction conditions must be adjusted to a pH range of 3–4 so that the resulting thorium hydroxide will precipitate from the solution.

Table 19.1: Uses for thorium or thorium compounds.

Form of thorium	**Uses**
Th metal	Magnesium–thorium alloys for aircraft or rocket components (Mg–Th)
ThF_4	Antireflecting material in multilayered optics
ThO_2 (thoria)	Ammonia → nitric acid catalyst
ThO_2	Ceramics, high temperature
ThO_2	Glass additive, for high precision lenses
	Gas lamps, camping lantern mantels

ThO_2	Gas lamps, camping lantern mantels
ThO_2	Gas tungsten arc welding

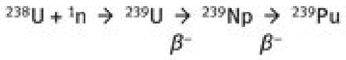
19.3 Uses

While energy production remains a potential use for thorium, it is currently also used in a variety of other ways, including: “catalysts, high temperature ceramics, and welding electrodes” (USGS, 2013). These are all smaller, niche applications, but they do have the potential for growth. Table 19.1 gives a summary of other uses for refined thorium, as well as for thorium-containing materials.

Thorium tetrafluoride is prepared from the direct combination of the metal with fluorine gas. Thoria is often a by-product of other extraction chemistry, but it becomes a useful material because of its very high melting point.

19.4 Potential uses for power

All the existing nuclear power plants throughout the world function with enriched uranium (^{235}U) as fuel. Some have claimed that the reason for this is simply because the different governments that worked on nuclear weapons during the Second World War assembled teams of scientists and engineers who realized that the same enriched fuel, at a slightly lower level of enrichment, could be used to heat water, turn turbines, and thus produce electrical power from uranium’s nuclear decay (The International Thorium Energy Organization, 2014; Martin and Richard, 2013). These same sources usually point out that thorium is the more plentiful of the two actinides, and that it is difficult for thorium to produce plutonium – an element used in nuclear weaponry that is produced through beta-particle emission from uranium. The production of plutonium from uranium, usually ^{238}U, is not a single-step process, but it does occur in fuel rods rather regularly. It involves a neutron absorption and two beta-particle emissions. The reaction chemistry can be represented in a straightforward manner, as shown in Figure 19.3.



$$^{238}U + {}^{1}n \rightarrow {}^{239}U \underset{\beta^-}{\rightarrow} {}^{239}Np \underset{\beta^-}{\rightarrow} {}^{239}Pu$$

Fig. 19.3: Plutonium production.

The use of thorium as fuel for nuclear power generation would in theory eliminate this transmutation pathway, and thus make the waste material from reactors much safer than that which currently exists.

19.5 Recycling

Thorium end uses in consumer materials mean that it is widely distributed into small items in such a manner that there is currently no financial need to recycle thorium. Should thorium be used as a fuel in any future nuclear reactor, disposal plans will have to be formulated for the fuel when it nears the end of its usable lifetime.

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20 Catalysts

Practically every general chemistry book used in secondary schools or colleges gives some space to the basic principles of catalysis. Such discussions always include the idea that a catalyst must speed up a reaction, and at the same time not be consumed in the reaction. Catalysts are generally divided into two categories: heterogeneous and homogeneous. Heterogeneous catalysts are not in the same phase as the reaction with which they interact, while homogeneous catalysts are. Less discussed are the costs of the catalyst itself, the ease of use, or the ease of recovery.

Despite a wide variety of catalysts that exist, or perhaps because of it, there is no single theory that encompasses why all catalysts function. Almost always, the use of a catalyst is an empirical decision, one that helps a reaction proceed. The field of catalyst chemistry is so wide that there are several societies devoted to it (The International Association of Catalysis Societies, 2014; Acmite Market Intelligence, 2014) which continue to examine mature as well as new reactions for possibilities concerning catalyst use.

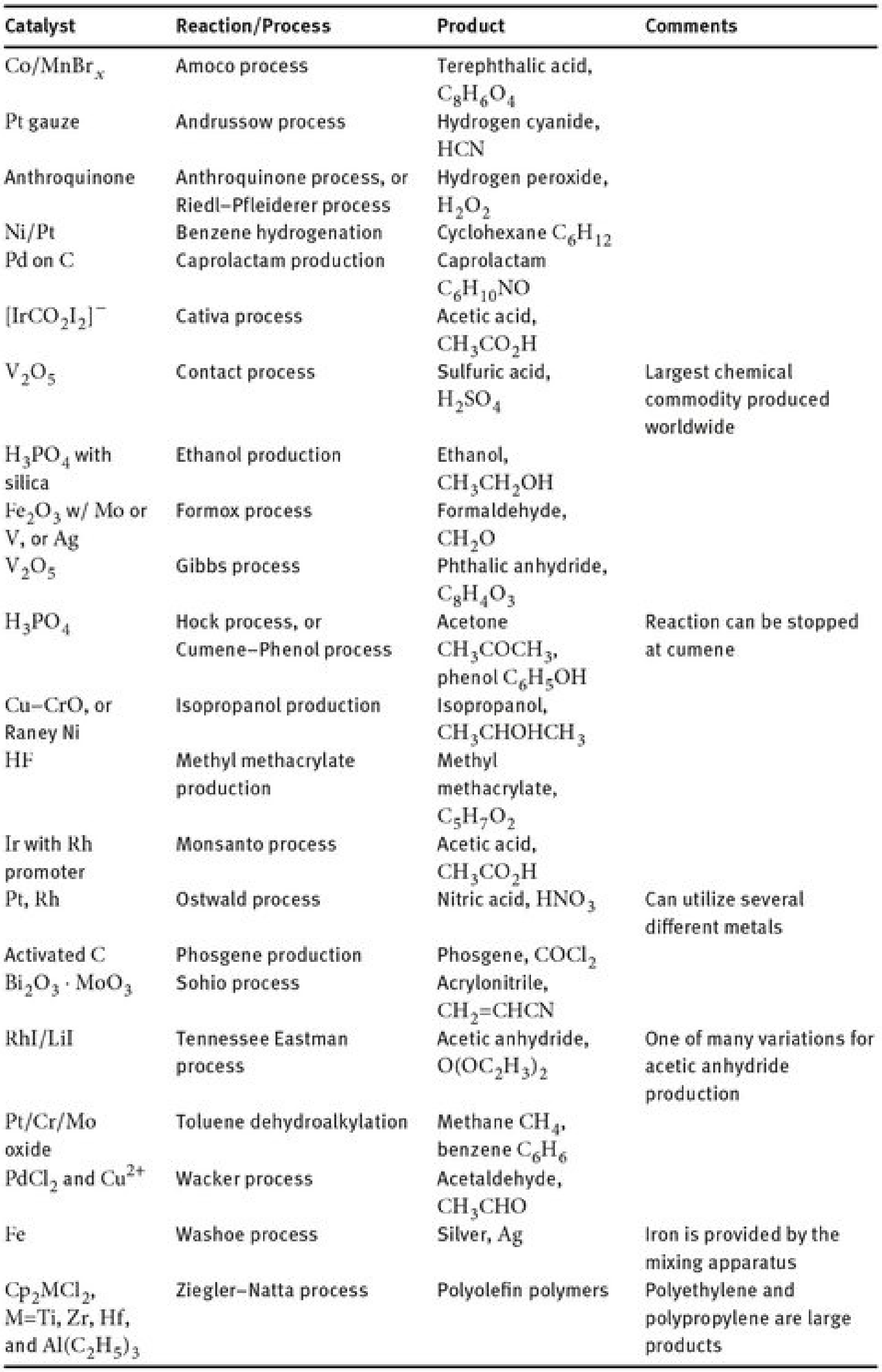
20.1 Uses

Since there is no overarching theory for the production and application of catalysts, it is probably useful to simply tabulate several more industrially useful catalysts. Table 20.1 is a nonexhaustive list that shows many of the common catalysts used in different sectors of the chemical industry and the reactions with which they are associated. The organization is simply an alphabetical one, based on the name of the reaction or process.

20.2 Syntheses

The simpler catalysts shown in Table 20.1 are materials which are themselves made in large quantities. There are however some catalysts that are produced much like fine chemicals. These may cost more than other catalysts, but the cost savings in making the bulk chemical with which they are associated makes the cost of the actual catalyst more affordable. Also, there is an enormous number of catalysts that have been proven useful for a reaction or class of reactions that have not been utilized for one of the industrial scale reactions discussed in this book (Strem Chemicals, 2014).

Table 20.1: Industrial processes and reactions incorporating catalyst.



Catalyst	Reaction/Process	Product	Comments
Co/$MnBr_x$	Amoco process	Terephthalic acid, $C_8H_6O_4$	
Pt gauze	Andrussow process	Hydrogen cyanide, HCN	
Anthroquinone	Anthroquinone process, or Riedl–Pfleiderer process	Hydrogen peroxide, H_2O_2	
Ni/Pt	Benzene hydrogenation	Cyclohexane C_6H_{12}	
Pd on C	Caprolactam production	Caprolactam $C_6H_{10}NO$	
$[IrCO_2I_2]^-$	Cativa process	Acetic acid, CH_3CO_2H	
V_2O_5	Contact process	Sulfuric acid, H_2SO_4	Largest chemical commodity produced worldwide
H_3PO_4 with silica	Ethanol production	Ethanol, CH_3CH_2OH	
Fe_2O_3 w/ Mo or V, or Ag	Formox process	Formaldehyde, CH_2O	
V_2O_5	Gibbs process	Phthalic anhydride, $C_8H_4O_3$	
H_3PO_4	Hock process, or Cumene–Phenol process	Acetone CH_3COCH_3, phenol C_6H_5OH	Reaction can be stopped at cumene
Cu–CrO, or Raney Ni	Isopropanol production	Isopropanol, $CH_3CHOHCH_3$	
HF	Methyl methacrylate production	Methyl methacrylate, $C_5H_7O_2$	
Ir with Rh promoter	Monsanto process	Acetic acid, CH_3CO_2H	
Pt, Rh	Ostwald process	Nitric acid, HNO_3	Can utilize several different metals
Activated C	Phosgene production	Phosgene, $COCl_2$	
$Bi_2O_3 \cdot MoO_3$	Sohio process	Acrylonitrile, $CH_2{=}CHCN$	
RhI/LiI	Tennessee Eastman process	Acetic anhydride, $O(OC_2H_3)_2$	One of many variations for acetic anhydride production
Pt/Cr/Mo oxide	Toluene dehydroalkylation	Methane CH_4, benzene C_6H_6	
$PdCl_2$ and Cu^{2+}	Wacker process	Acetaldehyde, CH_3CHO	
Fe	Washoe process	Silver, Ag	Iron is provided by the mixing apparatus
Cp_2MCl_2, M=Ti, Zr, Hf, and $Al(C_2H_5)_3$	Ziegler–Natta process	Polyolefin polymers	Polyethylene and polypropylene are large products

20.2.1 Metallocenes

The metallocene catalysts can be categorized as those which must be synthesized, as opposed to refined or purified from some natural source. A sample reaction whereby a metallocene catalyst is formed is shown in Figure 20.1.

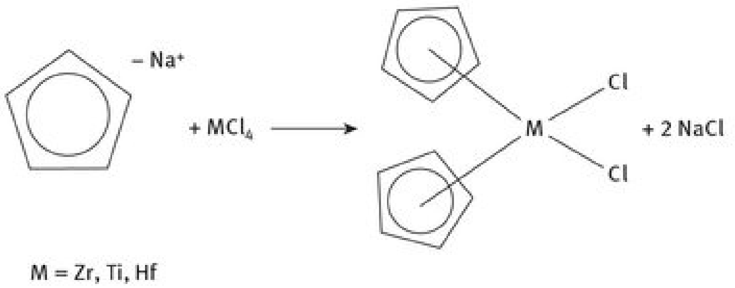


Fig. 20.1: Production of Metallocene Catalysts.

The number of metallocene catalysts is great, with different metal centers, and different organic ring components. The organic fraction shown in Figure 20.1, cyclopentadiene (abbreviated Cp), is usually refined and produced ultimately as part of petroleum distillation, but a wide variety of substituted Cp molecules must oftentimes themselves be synthesized. The success of Ziegler–Natta catalysis has fueled numerous research efforts in the past decades into reactions for which these catalysts might find some applicability.

20.2.2 Zeolites

This class of aluminosilicate materials is often used as catalysts for specific reactions, and usually they take advantage of a large surface area on which substrate molecules can react. But in the past 30 years, numerous zeolites have been manufactured. This is often done in what is called a sol–gel system, in which crystalline surfaces are grown slowly under precise pH conditions. The solution portion – the sol – is often a colloidal solution, and the final material is in the gel phase.

20.3 Recycling

Catalyst recycling is not something that involves an end-use product. Rather, the cost of a specific catalyst is usually enough that it is economically feasible to try to recover it from any end product, be it a plastic, or a bulk commodity, such as nitric acid. Table 20.1 illustrates how many expensive metals are used in different reactions, all of which are recovered from their reaction systems when possible.

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21 Bromine

Bromine, a halogen that when isolated takes the form of a toxic red–brown liquid with a strong odor (the name is derived from the Greek word for “stench”), is a relatively rare element, but one that has found several uses in the chemical industry. It does not have a particularly long history, having only been isolated in 1825–1826. But it quickly became a commodity chemical, with Dow Chemical extracting it before the turn of the twentieth century (First Commercial Production of Bromine, 2014; Dow Chemical Company, 2014).

21.1 Mining and sources

Bromine is neither found widely in different minerals nor found in nature as a free element. Because the bromide ion is quite soluble in water, bromides can be concentrated from brine solutions, and then extracted from them. Bromide exists in seawater in concentrations as high as 65 ppm; it also occurs at much higher concentrations in certain brines at various locations throughout the world. Figure 21.1 shows the most recent data for bromine production by country. The United States is excluded from the figure because the two companies that manufacture it in the country did not wish to disclose proprietary data (USGS, 2013).

The total worldwide annual output is almost 600,000 metric tons. Both Israel and Jordan extract bromine as bromide from their shared body of water and boundary, the Dead Sea. The salinity of this small, endorheic sea is roughly nine times greater than that of the oceans. The United States extracts bromine from wells in the southern counties of the state of Arkansas (Albermarle Chemical Company, 2014) as well as from Michigan (Dow Chemical Company, 2014). Japan and China extract it from seawater, as do most other nations, through large evaporation ponds or pools. In all cases, some concentration of the existing brine must be accomplished to make the recovery of bromine economically profitable.

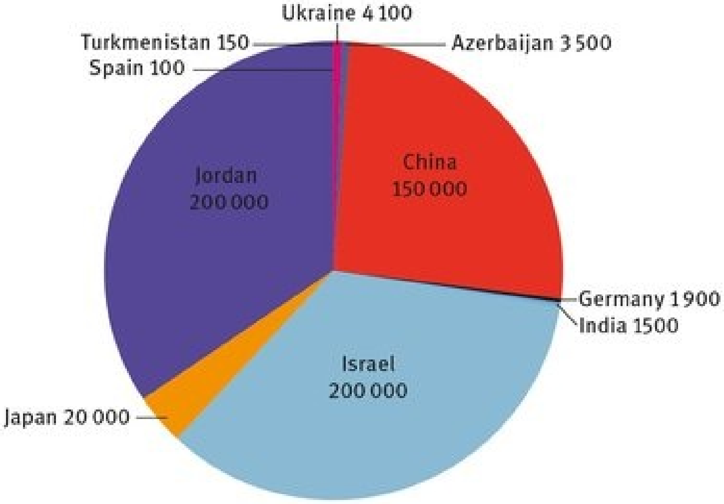


Fig. 21.1: Global bromine production, in metric tons (USGS, 2013).

21.2 Extraction chemistry

The isolation of bromine from bromide-containing brines is the major way by which the element is isolated. Although there are methods which start with hydrobromic acid (HBr) or sodium bromide (NaBr), these are small in scope, and not utilized on an industrial scale.

Bromine refining and isolation depends on the availability of chlorine, which is much more common halide and halogen. The brines must be concentrated, but not dried, and then have chlorine gas flushed through them along with air. Chlorine is thus reduced to the anion, while bromide is oxidized to the free element. The reaction chemistry can be shown very simply, as depicted in Figure 21.2.

$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-$$

Fig. 21.2: Bromine isolation.

The earliest commercial production of bromine was an electrolytic process pioneered by Herbert Dow, who with the help of his process found the Dow Chemical Company in Michigan, USA in 1897. At the same time when Mr. Dow was producing bromine, he was also producing and using chlorine, as both elements were found in the brine wells that served as the point source for bromine (First Commercial Production of Bromine, 2014).

Large amounts of elemental chlorine are produced in what is called the chlor-alkali process, which can operate in three somewhat different configurations. Sodium hydroxide is often considered the main product of that process, chlorine is the second, and hydrogen gas is a third isolable product. Chlorine is also produced in Downs cells, as a co-product in the production of elemental sodium, which was discussed in Chapter 16.

21.3 Uses

Bromine finds a very diverse suite of uses in industry and in consumer end-use products. Curiously, the ease with which the carbon–bromine bond can be broken is what has made organo-bromides very useful materials in flame retardants. The resulting radical combines with those formed in combustions, and thus shuts the combustion down. Unfortunately, in the atmosphere, these bromine radicals can react with ozone, with the overall affect being a weakening of the ozone layer. For that reason, continued efforts are made to find replacement materials that do not contain bromine for use as flame retardants and fumigants.

21.3.1 Flame retardants

While there are several major uses for bromine, the series of end-products that occupy the largest market share are flame retardants. The bromine–carbon bond in brominated organic compounds is weaker than a hydrogen–carbon covalent bond, and when broken, tends to form a radical. As mentioned, these radicals are able to suppress those produced during combustion. Thus, brominated compounds find use in flame and fire retardants. There are a large number of these compounds, but some of the common ones are:

- Decabromodiphenyl ethane
- Decabromodiphenyl ether (decaBDE)
- Brominated polystyrene
- Hexabromocyclododecane
- Tetrabromobisphenol A
- Tetrabromophthalic anhydride

These and other poly-brominated compounds can be produced through direct addition of bromine or HBr to the organic starting molecule (Albermarle Chemical Company, 2014). Small amounts of them are often added to large volume plastics until the desired level of flame retardant ability is met. For example, hexabromocyclododecane is usually added to polystyrene in less than 10% by volume, because its flame retarding ability is quite high.

Lewis structures of these flame retardants are shown in Figure 21.3.

The United States Environmental Protection Agency and corporate producers of brominated flame retardants have agreed that decaBDE will no longer be manufactured in the United States by the end of 2013. The reason was concern over breakdown products and their effects on human health (USGS, 2013).

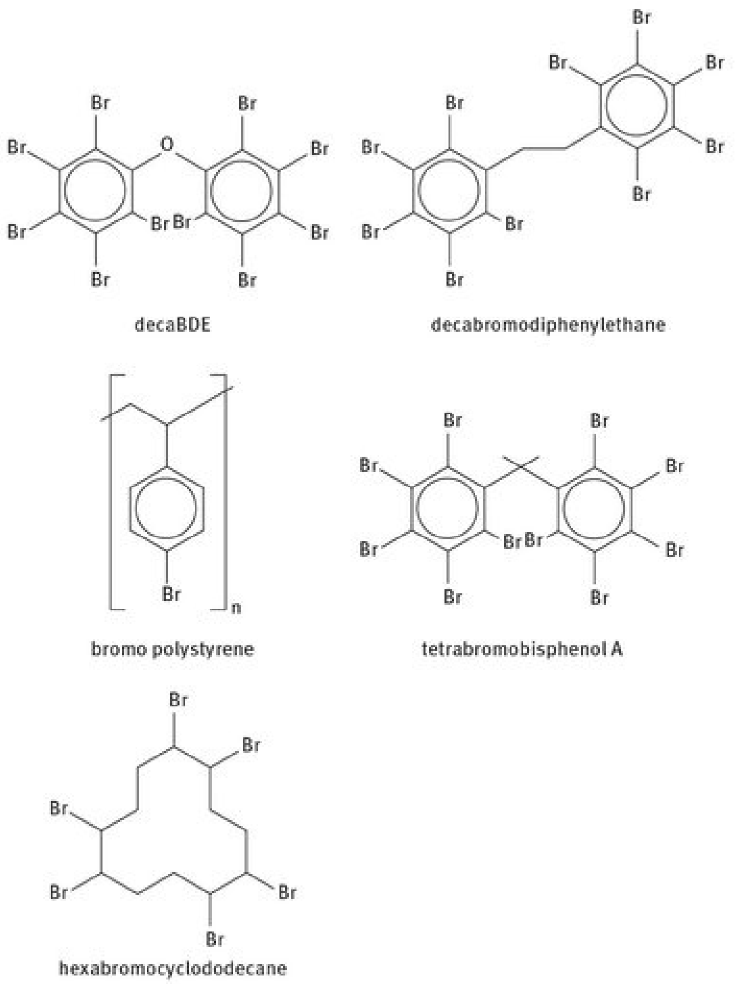


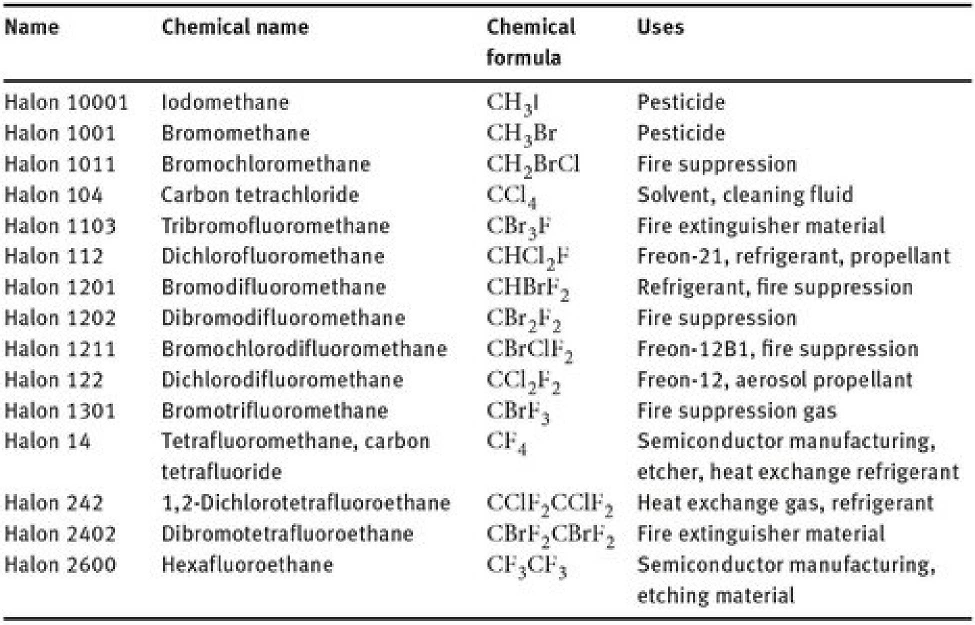
Fig. 21.3: Lewis structures of several flame retardants.

21.3.2 Halons

The term “halons” indicates a series of short-chain alkanes that contain one or more types of halogen, often including bromine. Several of them have not only been used as flame retardants, but they also find use as dry-cleaning fluids and in other agricultural applications. Table 21.1 lists several of the halons that have been made on a commercial scale, as well as their uses.

It can be seen that of the 15 halons listed here, eight have at least one bromine atom in their formula. While many of these make effective fire suppression materials or pesticides, many of the halons have been banned for public use in the past 10 years, because they and their breakdown products are known to be ozone-depleting materials.

Table 21.1: Halons and their uses.



Name	Chemical name	Chemical formula	Uses
Halon 10001	Iodomethane	CH_3I	Pesticide
Halon 1001	Bromomethane	CH_3Br	Pesticide
Halon 1011	Bromochloromethane	CH_2BrCl	Fire suppression
Halon 104	Carbon tetrachloride	CCl_4	Solvent, cleaning fluid
Halon 1103	Tribromofluoromethane	CBr_3F	Fire extinguisher material
Halon 112	Dichlorofluoromethane	$CHCl_2F$	Freon-21, refrigerant, propellant
Halon 1201	Bromodifluoromethane	$CHBrF_2$	Refrigerant, fire suppression
Halon 1202	Dibromodifluoromethane	CBr_2F_2	Fire suppression
Halon 1211	Bromochlorodifluoromethane	$CBrClF_2$	Freon-12B1, fire suppression
Halon 122	Dichlorodifluoromethane	CCl_2F_2	Freon-12, aerosol propellant
Halon 1301	Bromotrifluoromethane	$CBrF_3$	Fire suppression gas
Halon 14	Tetrafluoromethane, carbon tetrafluoride	CF_4	Semiconductor manufacturing, etcher, heat exchange refrigerant
Halon 242	1,2-Dichlorotetrafluoroethane	$CClF_2CClF_2$	Heat exchange gas, refrigerant
Halon 2402	Dibromotetrafluoroethane	$CBrF_2CBrF_2$	Fire extinguisher material
Halon 2600	Hexafluoroethane	CF_3CF_3	Semiconductor manufacturing, etching material

21.3.3 Fumigants

The compound 1,2-dibromoethane, more commonly known as ethylene bromide (an analog to 1,2-dichloroethane, historically also called Dutch liquid) is easily prepared from ethylene, and has found wide use as a fumigant for various insects. The reaction chemistry for its formation can be seen in Figure 21.4.

$$Br_2 + CH_2CH_2 \rightarrow BrCH_2CH_2Br$$

Fig. 21.4: 1,2-Dibromoethane production.

This compound also found use in leaded fuels, where the bromine combined with lead to create lead(II) bromide. This was phased out when leaded automobile fuels were replaced with the current unleaded fuels.

This compound was also used as an insecticide in various crop applications, but has generally been replaced by other, less toxic insecticides.

Methyl bromide found a specific niche use as a pesticide in the production of strawberries, enabling maximum strawberry growth. It too has been phased out, in part because improper, liberal spraying of it is believed to have caused three fatalities among farm workers in southern California. Its production requires methanol and hydrobromic acid, and can be written fairly simply, as shown in Figure 21.5.

$$HBr + CH_3OH \rightarrow CH_3Br + H_2O$$

Fig. 21.5: Methyl bromide production.

Several other bromine-containing pesticides that have been produced on an industrial scale have been listed in Table 21.1.

21.3.4 Drilling fluids

Bromine is combined with metals such as zinc, sodium, or calcium because the resulting solutions made from the salts are dense and useful as oil drilling solutions. InIn general, the additives in drilling fluids keep the drill from overheating or help keep the cuttings and materials suspended by raising the viscosity of the fluid.

21.3.5 Vegetable oil

Brominated vegetable oil (sometimes abbreviated BVO) is a food additive, mentioned in Chapter 11, which is added in small amounts to soft drinks. When added at the level of a few parts per million, BVO helps solubilize citrus flavors in soft drinks. Several countries have banned the production of soft drinks using BVO as an ingredient, citing health problems by consumers who ingest large amounts of such beverages. Consumers do know when BVO is in a product however, because it is listed in the ingredients. Figure 21.6 shows a bottle of Mountain Dew® with BVO listed as the second to the last ingredient. This means that it is the second to the smallest amount of ingredient present in the beverage.

Overall, the use of bromine for BVO is much smaller than that for other applications, such as flame retardants.

Fig. 21.6: Bottled Mountain Dew with brominated vegetable oil as ingredient.

21.4 Reuse and recycling

The recycling of bromine is possible in large enough industrial processes. The USGS Mineral Commodity Summaries 2013 makes the interesting statement:

> Some bromide solutions were recycled to obtain elemental bromine and to prevent the solutions from being disposed of as hazardous waste. Hydrogen bromide is emitted as a byproduct in many organic reactions. Plastics containing bromine flame retardants can be incinerated as solid or-organic waste, and the bromine can be recovered (USGS, 2013).

While this does not explain the chemistry involved in the recycling processes, it implies that the driver for such recycling programs is economic. Specifically, there are cost savings when brominated material does not have to be disposed of – and paid for – as hazardous waste.

Bromine-containing materials also find use as a sorbent material in coal-fired power plants, in scrubbing mercury out of the effluent stacks (VGB PowerTech, 2014). While this is not a form of bromine recycling, it is an example of bromine being used toto capture another material that is considered dangerous to human and environmental health when released. Abatement of mercury emission from power plants continues to be an area of concern.

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22 Fluorine

The lightest of the halogens, fluorine is the one that was isolated last, although its compounds have been used for centuries. Because of its incredibly high reactivity, elemental fluorine never occurs freely in nature and proved to be extremely difficult to isolate. Indeed, although hydrofluoric acid, HF, was known in the nineteenth century, attempts to oxidize the fluorine to the free element from either HF or any fluoride-bearing ore proved elusive, and in several cases had harmful consequences to those experimenting with it. There is more than one injury and fatality associated with attempts throughout the nineteenth century to isolate the element. These individuals are today sometimes referred to as the fluorine martyrs.

Even today, elemental fluorine and hydrofluoric acid must be stored in plastic containers, as the materials etch glass, and thus would destroy glass containers. Despite this high reactivity, fluorine has become an extremely useful element, finding uses in applications as different as aluminum refining and the clothing industry. Several modern processes and products would not exist without the direct or indirect incorporation of fluorine, hydrofluoric acid, or some fluoride salt.

22.1 Isolation and production

Fluorine exists in the reduced form as fluoride in a wide variety of minerals. Three compounds, fluorite (CaF_2), cryolite (Na_3AlF_6), and fluorapatite ($Ca_5(PO_4)_3F$), are the main materials that are mined, from which fluorine or HF is extracted. Fluorite is so common that it can be found on all the inhabited continents (although only in small quantities in Australia) (Government of Southern Australia, 2014), but the fluorine or hydrofluoric acid extracted from it is now so crucial in several end applications that it is tracked by the United States Geological Survey Mineral Commodities Summary each year under the more common name “fluorspar” (USGS, 2014). The worldwide mine production of fluorite is shown in Figure 22.1. The United States is not listed, even though the figures are compiled from the USGS Mineral Commodities Summary, because of proprietary concerns (USGS, 2014).

The reaction chemistry that describes the isolation of elemental fluorine can be represented simply, as shown in Figure 22.2. While the reactions appear to be simple, there are numerous details that are essential to their successful functioning which are not easily expressed in a chemical equation. The reaction is an electrolysis, runs at low temperature (roughly 70–130 °C), uses platinum–iridium electrodes and surfaces (because the alloy is more resistant to corrosion than platinum alone), and originally utilized fluorite stoppers, again because they were resistant to the elemental product.

Fluorine was first isolated by Henri Moissan in 1886. Although there has recently been a published report of a chemical isolation of fluorine, industrial scale manufacturing of the element is not very much changed from that which gave Moissan his early success (he actually received the Nobel Prize in 1906 for this work).

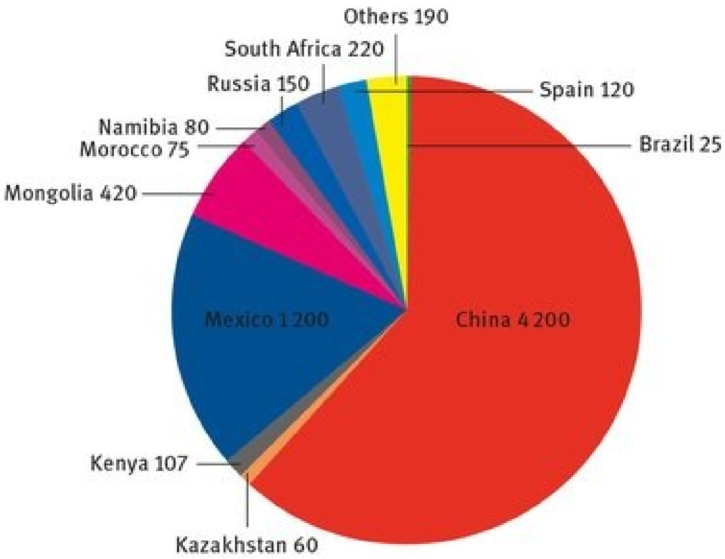


Fig. 22.1 **:** Worldwide fluorite production (in thousands of metric tons).

$$KF + HF \rightarrow KHF_2$$
followed by:
$$2\,KHF_2 \rightarrow F_{2(g)} + H_{2(g)} + 2KF$$

Fig. 22.2: Elemental fluorine isolation.

Elemental fluorine finds some industrial scale use, specifically in producing UF_6 and SF_6 for uranium enrichment and electrical insulation, respectively. The reaction chemistry can be represented as additions, shown in Figure 22.3.

$$U + 3\,F_{2(g)} \rightarrow UF_{6(g)}$$
and
$$S + 3\,F_{2(g)} \rightarrow SF_{6(g)}$$

Fig. 22.3: UF_6 and SF_6 production.

Gaseous UF_6 is used to concentrate U-235, which is the fissile isotope of uranium, but a small percentage of all uranium isotopes. Sulfur hexafluoride is used as a dielectric medium and is made on a scale of several thousand tons annually.

22.2 Hydrogen fluoride

In a large number of applications, elemental fluorine is not required to make a fluorinated product. Instead, hydrogen fluoride (HF) is used as the starting material. Hydrogen fluoride can be produced from the mineral fluorite – fluorspar – upon treatment with sulfuric acid. The reaction chemistry is straightforward, and is shown in Figure 22.4.

$$H_2SO_{4(aq)} + CaF_{2(s)} \rightarrow 2\ HF_{(g)} + CaSO_{4(s)}$$

Fig. 22.4: Production of hydrofluoric acid.

The resulting HF is usually refined to two different levels of purity, each of which goes by a nonsystematic name. Acidspar is roughly 97% purity HF, and it is used for the production of fluorinated carbon-based materials, for the production of synthetic cryolite needed for aluminum refining, or for steel production. A small amount is refined to fluorine gas and combined with uranium for isotopic uranium enrichment. What is called metspar varies in purity from approximately 65–85%, and is used, with rare exception, for the smelting of iron. The two grades are produced in roughly equal amounts annually.

22.3 Cryolite

While cryolite can be a minable mineral, it is now rare; and the mine at Ivigtut, Greenland closed in 1987 because the ore was depleted beyond the point where extraction was profitable. Thus, synthetic cryolite has replaced mined ore as the source of the cryolite used in aluminum smelting. This can be made to high purity, and thus does not need the purification treatment that mined ores often do. The reaction chemistry illustrating the production of synthetic cryolite can be shown in Figure 22.5.

$$3\ NaOH + 6\ HF + Al(OH)_3 \rightarrow Na_3AlF_6 + 6\ H_2O$$

Fig. 22.5: Cryolite synthesis.

This leads to a large use of sodium hydroxide, which is itself one of the largest production inorganic chemicals in the world.

The reaction also requires a significant outlay of electrical energy. It requires at least 10,000 A and 4.5 V for the synthesis. A comparison is useful, when looking at cryolite, to see what commodities are required in aluminum production. What is required for 1 ton of aluminum is:

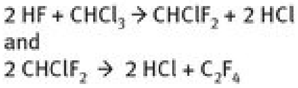
1. 1.89 tons of Al_2O_3
2. Roughly 0.45 tons of carbon anode material
3. 0.07 tons of Na_3AlF_6
4. 15,000 kWh of electricity

Clearly, while cryolite is required for aluminum production, electrical power becomes the major expense (Greenwood and Earnshaw, 1980; Alcoa, 2014).

22.4 Teflon

Numerous halogenated carbon-based molecules have been produced in the past century, with those known as the chlorofluorocarbons finding uses as refrigerant gases and several other applications. But Teflon, more properly polytetrafluoroethylene (PTFE), produced from tetrafluoroethylene in a standard olefin polymerization that also requires hydrofluoric acid, has become a polymer that has changed the world in several ways.

Tetrafluoroethylene, the starting material for Teflon, in turn is produced from chloroform, according to the reactions as shown in Figure 22.6.



$2\,HF + CHCl_3 \rightarrow CHClF_2 + 2\,HCl$

and

$2\,CHClF_2 \rightarrow 2\,HCl + C_2F_4$

Fig. 22.6: Production of tetrafluoroethylene.

Clearly hydrofluoric acid is one of the reactants. Chloroform itself is made from the reaction of methane with chlorine gas, and thus the ultimate starting material for tetrafluoroethylene is natural gas.

The co-product hydrochloric acid must be captured for further use and is generally not discarded.

The story of the discovery and development of Teflon is one of the scientific successes of the 20th century, as well as one in which both serendipity and tragedy have a place. The discoverer of the material, Dr Roy Plunkett, found in 1938 while working for DuPont that a tank of tetrafluoroethylene he had planned to use in an experiment had polymerized in its tank. He was keen enough to isolate and identify the newly polymerized material, PTFE. The material, inadvertently produced at a laboratory scale, proved to be both highly corrosion resistant and rather expensive. The advent of the Second World War, and the need for corrosion resistant materials during the isolation of isotopically enriched uranium in the form of UF_6 gas meant that the scale-up of PFTE became imperative for the war effort. Brigadier General Leslie Groves is credited for insisting that the isotopic enrichment tubing and equipment used in the Manhattan Project be changed from nickel metal, which did corrode to some extent in the purification process, to Teflon-lined tubing surfaces, which did not corrode in the presence of UF_6 gas.

The reaction chemistry showing the production of Teflon from its monomer can be represented as shown in Figure 22.7. The polymerization is a free radical one, and the reaction can run at low temperatures (as evidenced by Plunkett's original discovery).

The common perception is that Teflon is now used mainly as a coating on frying pans and other cookware, but the profile of uses for this per-fluorinated polymer is much wider than this. The DuPont website states:

> Today, Teflon® coatings, and additives are used in paints, fabrics, carpets, home furnishings, clothing and so much more (DuPont, 2014).

While this is certainly a corporate perspective with a bias toward their products and materials, it does correctly indicate that Teflon finds extensive use in a variety of consumer products and materials, including fabrics.

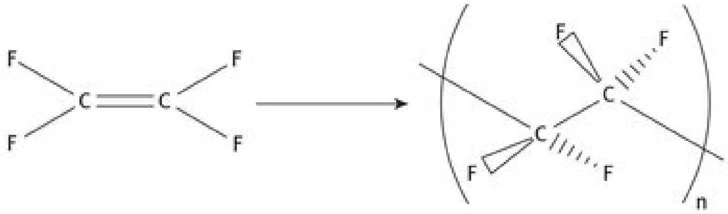


Fig. 22.7: Production of polytetrafluoroethylene.

22.5 Fluorinated fibers

Polytetrafluoroethylene has, in the past decades, become a valuable material in waterproof, outdoor clothing and in other fabrics for which the repelling of water is a major concern. The trade name Gortex® has become synonymous with such clothing in the minds of many (WL Gore & Associates, 2014). This fabric is made from PTFE that has been thermomechanically expanded and bonded to a base fabric.

The WL. Gore & Associates company continues to produce and market several other materials besides Gortex, which according to the corporate website includes: cables and cable assemblies, electronic and electrochemical materials, fabrics, fibers, filtration products, medical products, pharmaceutical processing, pump tubing, sealants, and venting products (WL Gore & Associates, 2014).

22.6 Dental fluoride and fluoridated water

In the past 60 years, the addition of small amounts of fluoride to drinking water in some countries (levels generally range from 0.5 to 1.0 mg/L) is believed to have helped reduce the number of cavities in the population. The advent of fluoridated toothpastes has also led to the decrease of cavities in the general population, especially in children. Ironically, the advent of fluoridated toothpastes coupled with this decline in cavities has actually led to calls for the removal of fluoride from drinking water, in part because of concerns that too much fluoride has been added in the water of some communities, and the belief that the fluoride supplied in toothpaste is more specifically targeted.

The debate about fluoride use in water and in communities can be quite heated, and at least one book, *The Fluoride Deception*, by Christopher Bryson, has been written about the subject, exploring it in detail (Bryson, 2004; International Society for Fluoride Research, 2014).

22.7 Recycling and reuse

The recycling of fluorine-containing materials is generally not something with which consumers are concerned, as they might be with such products as paper, aluminum cans, or glass and plastic bottles. Yet fluorides are often monitored closely and reused as much as possible, usually for economic reasons. For example, once cryolite has been synthesized, it is cost-effective to ensure its reuse in aluminum production for as long as possible.

Also, as one might expect, the accidental release of fluorine, hydrofluoric acid, and fluoride-containing materials can be deadly, and thus tight controls as well as continued reuse are common where these materials are concerned.

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23 Glass

Broadly defined, glass is any amorphous material which can exist in a hard, usually brittle state as well as in a molten, generally soft but viscously liquid state, and that can be transformed from one to the other repeatedly. Most people think of glass in less technical terms, considering it to be in some way a transparent, hard, brittle material that is not metallic. Using this as a broad definition, glass could be a polymer, such as a polycarbonate. This chapter will focus only on traditional glass, meaning the material made from silica and other inorganic materials.

23.1 Raw materials

Most glass requires three materials: silicon dioxide (sometimes just called sand, although it must be quite free of impurities), soda ash, and calcium oxide, still often called lime. These three materials are so common that glass can be produced in almost any country. The United States Geological Survey does not track glass in its Mineral Commodity Summaries which are published each year, but does track all three of the above ingredients, sand, soda ash, and lime (USGS, 2013). Of the three, soda ash finds its largest use in glass making. Perhaps obviously, sand sees much larger volume uses in construction and cement making and lime sees its major use in steel manufacturing.

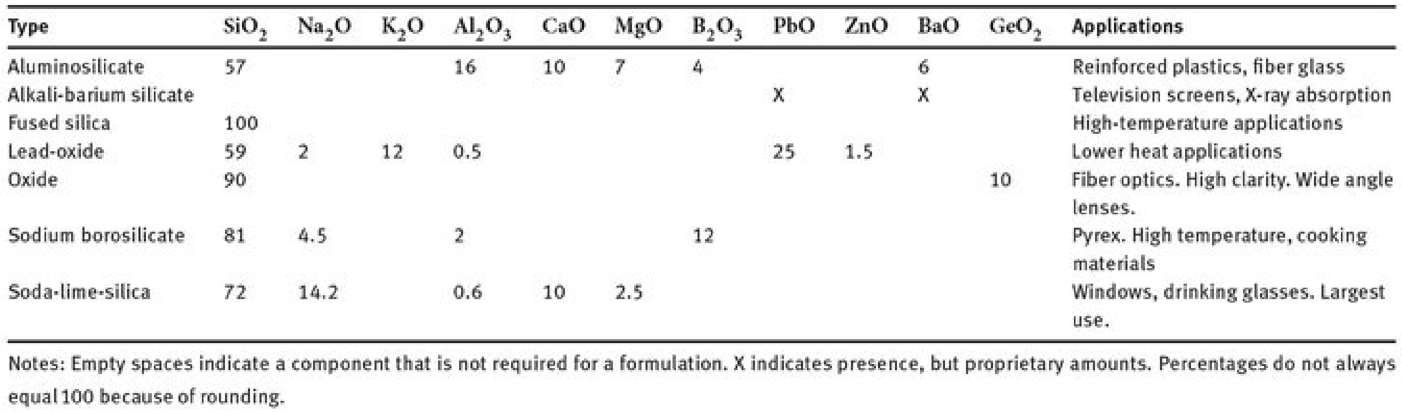
23.1.1 Compositions

Various other materials are added to glass mixtures, always to change one property or another, to arrive at a material with some desired combination of properties and abilities. Examples of several different types of glass are shown in Table 23.1.

Numbers indicate percentages of components.

While this variety of glass types shows the versatility of it as a material, soda-lime-silica glass is the formulation used on the largest scale by far. Production and sales do change from one year to the next, but roughly 90% of glass manufacturing is for this type. There are also several types of glass made in smaller quantities, for niche uses. Overall though, glass is used on such a large scale that several trade organizations exist which are devoted to the manufacture, sale, and use of numerous types of glass (Glass Association of North America, 2014; National Glass Association, 2014; Glass Manufacturing Industry Council, 2014; Glass Build America, 2014; British Glass, 2014; Bundesverband Glasindustrie, 2014; Glass Alliance Europe, 2014).

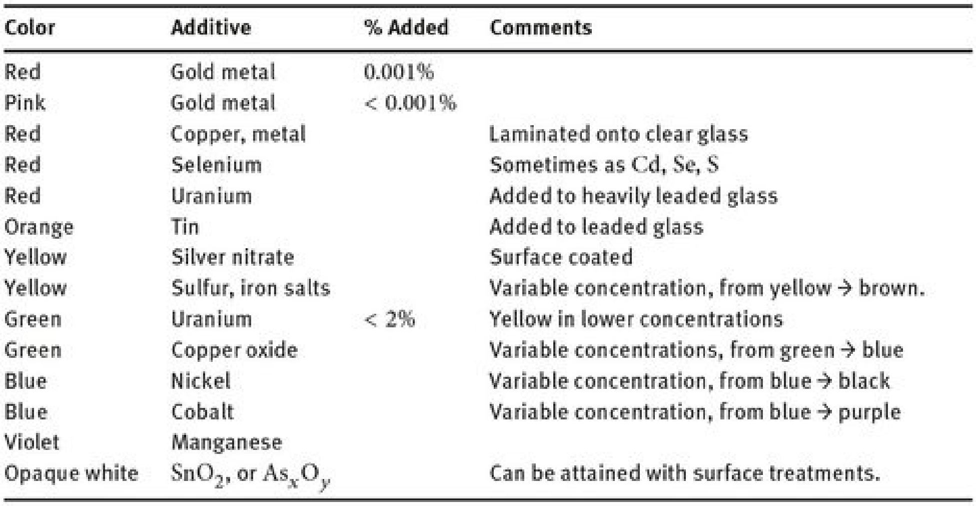
Table 23.1: Common types of glass.



Type	SiO_2	Na_2O	K_2O	Al_2O_3	CaO	MgO	B_2O_3	PbO	ZnO	BaO	GeO_2	Applications
Aluminosilicate	57			16	10	7	4			6		Reinforced plastics, fiber glass
Alkali-barium silicate								X		X		Television screens, X-ray absorption
Fused silica	100											High-temperature applications
Lead-oxide	59	2	12	0.5				25	1.5			Lower heat applications
Oxide	90										10	Fiber optics. High clarity. Wide angle lenses.
Sodium borosilicate	81	4.5		2			12					Pyrex. High temperature, cooking materials
Soda-lime-silica	72	14.2		0.6	10	2.5						Windows, drinking glasses. Largest use.

Notes: Empty spaces indicate a component that is not required for a formulation. X indicates presence, but proprietary amounts. Percentages do not always equal 100 because of rounding.

Table 23.2: Color additives for glass.



Color	Additive	% Added	Comments
Red	Gold metal	0.001%	
Pink	Gold metal	< 0.001%	
Red	Copper, metal		Laminated onto clear glass
Red	Selenium		Sometimes as Cd, Se, S
Red	Uranium		Added to heavily leaded glass
Orange	Tin		Added to leaded glass
Yellow	Silver nitrate		Surface coated
Yellow	Sulfur, iron salts		Variable concentration, from yellow → brown.
Green	Uranium	< 2%	Yellow in lower concentrations
Green	Copper oxide		Variable concentrations, from green → blue
Blue	Nickel		Variable concentration, from blue → black
Blue	Cobalt		Variable concentration, from blue → purple
Violet	Manganese		
Opaque white	SnO_2, or As_xO_y		Can be attained with surface treatments.

23.1.2 Colors

Various additives are incorporated into glass mixtures when they are molten or semi-molten to create specifically colored glasses. These are collectively referred to as “pot metal glass.” Others are applied to a surface, and then re-heated to fuse the colored layer to a clear base of glass. Glasses made in this fashion are called “flashed glass.”

Historically, churches have used these specialty, colored glasses in what are called stained glass windows, which are often made from large numbers of different colored, small panes of glass. This form of architectural adornment started in Europe, but has since spread throughout the world, and still occupies a niche in the glass making industry today.

Table 23.2 illustrates several additives that create various colors. Since there is no theory concerning how such colors form, the table simply lists them in the order of a rainbow using the old mnemonic for colors, Roy G. Biv, from red to violet.

The reason percentages are not listed for each color is that there is significant variation which produces a range of color (from red to yellow, for example), and the processes by which specific colors are produced are still proprietary in some cases.

23.2 Production

Although glass has been produced for millennia, there are still only two main ways to manufacture it. One, simply called glass blowing, goes all the way back to the origins of glass production, where it was used to make small bottles, cups, and other containers. While much of this is automated today, the process remains essentially the same.

What is called the “float glass process” is used to produce sheets of glass. This process is newer than glassblowing and can produce large sheets of glass of uniform thickness. The process was first tried in the 1950s by Sir Alastair Pilkington. For this reason, the process is also called the Pilkington Process (Pilkington, 2014). Glassblowing steps can be divided as follows:

1. *Batch house*. Mixing of the materials occurs in the batch house, as the materials are fed to the furnace.
2. *Furnace or hot end*. The furnace is where the raw glass is made molten, and items are formed and initially shaped, usually using a variety of molds. Most furnaces produce tons of glass products per day.
3. *Annealing*. As the glass cools, the object is fed into an annealing oven, so that the cooling is controlled and even. Some annealing operations can take more than a day of constant slow cooling.
4. *Cold end*. Final treatment of bottles and containers occurs at the cold end. This always includes an inspection of the bottle for defects, and may include the application of some outer coating to the glass.

Float glass differs in that the molten glass floats on a bed of molten tin (although other metals can be used) after any mixing in the furnace. The purpose of this step is to impart a uniform thickness to the glass.

Both processes are very energy intensive, requiring temperatures as high as 1750 °C. Since the processes are of large scale (a float glass factory can be several hundred meters long), oil or natural gas is used as the fuel source to obtain the temperatures required to melt the glass batches.

23.3 Uses

The uses of the various types of glasses are myriad. Window glass, bottles, and jars are three applications that come quickly to mind in terms of consumer products that are made from glass, but there are many other uses for glass or glass-like materials as well. A partial listing, quoting the Glass Alliance Europe website, states: “Glass is used in the following nonexhaustive list of products:

- Packaging (jars for food, bottles for drinks, flacon for cosmetics and pharmaceuticals)
- Tableware (drinking glasses, plate, cups, bowls)
- Housing and buildings (windows, facades, conservatory, insulation, reinforcement structures)
- Interior design and furnitures (mirrors, partitions, balustrades, tables, shelves, lighting)
- Appliances and Electronics (oven doors, cook top, TV, computer screens, smartphones)
- Automotive and transport (windscreens, backlights, light weight but reinforced structural components of cars, aircrafts, ships, etc.)
- Medical technology, biotechnology, life science engineering, optical glass
- Radiation protection from X-rays (radiology) and gamma-rays (nuclear)
- Fiber optic cables (phones, TV, computer: to carry information)
- Renewable energy (solar-energy glass, wind turbines)” (Glass Alliance Europe, 2014).

23.4 Reuse and recycling

Very few materials have as much of a reuse and recycling history as glass. Glass bottles for beverages have been recycled or reused for decades. In many cases, bottles are simply deposited into large containers. The containers are then sent to glass companies that have the capability of melting the batch and remaking bottles from the material. The term “cullet” is sometimes used for this type of recycled glass. In other cases, glass bottles are returned intact to a point of origin, often a store or business, then sent back to a bottling facility. There they are sanitized and reused.

Some countries have national programs for recycling glass bottles, while other nations leave policy to regional or state governments.

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24 Cement

As with several other large-scale chemical commodities, cement has an ancient history. People throughout the world have been using various mixtures of earth-based minerals to create substances that will act as binders, usually in the construction of buildings, walls, fortifications, or roads. Buildings from ancient times in China, south-west Asia, and parts of the Roman Empire all used some type of cement in their construction.

Only in the last few 100 years, however, has an experimental science for the formulation and production of cement been developed. The world as we know it today, with cities that have numerous high-rise buildings, roads that can be subjected to the stress of high speed, heavy traffic, and enormous hydroelectric power dams, would not be possible without the use of massive amounts of cement.

This chapter will discuss hydraulic cement, meaning cement that can set underwater, as well as nonhydraulic cement, which cannot do so. When the term “concrete” is used, it refers to mixtures of a type of cement that is further mixed with stone, sand, or other aggregate material to make some type of end product that can set in a specific, designed shape.

24.1 Sources

The source materials for cement are common throughout most of the world. The United States Geological Survey Mineral Commodity Summaries for 2013 does track cement production, but states:

> “Although individual plant reserves are subject to exhaustion, cement raw materials, especially limestone, are geologically widespread and

> abundant, and overall shortages are unlikely in the future (USGS, 2014).

The distribution of cement production countrywise as of 2012 is shown in Figure 24.1. Countries from which the United States imports cement include: Canada, South Korea, China, and Mexico (USGS, 2014).

While it is obvious that the output of cement in China is enormous, it can also be seen that cement is produced in large quantities in many other developed countries in the world. Indeed, there are several national and international trade associations devoted to the production, manufacture, sale, and research into cement and its uses (America's Cement Manufacturers, 2014; British Cement Association, 2014; Mineral Products Association, 2014; Verein Deutscher Zementwerke, 2014; Cembureau, 2014).

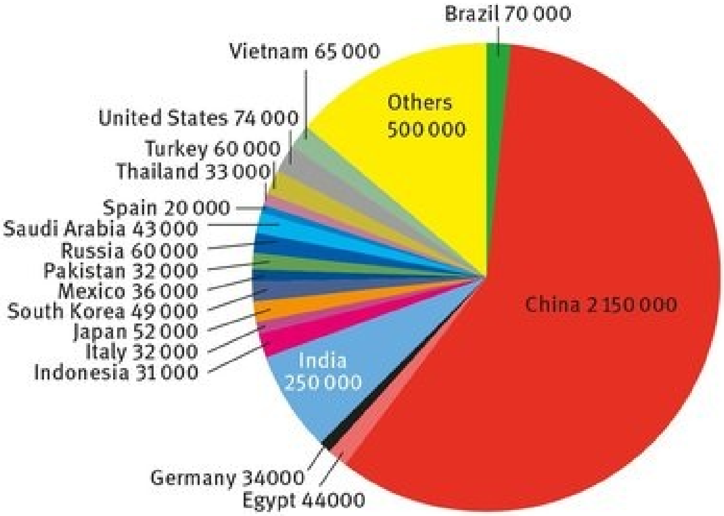

Fig. 24.1: Cement production, in thousands of metric tons.

24.2 Production and formulation chemistry

The production chemistry of various cements can be broken into two broad categories, based on whether or not the material in question can set underwater. As mentioned, any hydraulic cement is one that can set underwater, and any nonhydraulic cement does not. Hydraulic cements all require one or more materials that form sparingly soluble hydrates. Nonhydraulic cements require some carbon dioxide to set, which is usually just the carbon dioxide in the air.

24.2.1 Hydraulic cement chemistry

What is often called “Portland cement” requires one or more forms of mixed calcium–aluminum oxides. The steps in its manufacture can be broken down as follows, in what is called the “dry method”:

1. *Quarrying and crushing*. This is usually a mixture of limestone ($CaCO_3$) and clay that is brought down to particle size of 6–7 cm.
2. The addition of fly ash (SiO_2 and CaO) and iron ore to the mix.
3. Processing through an almost horizontal kiln, which reaches final temperatures of approximately 1500 °C. This drives off gaseous material and forms what is called clinker, pieces that are roughly 2 cm in diameter.
4. Cooling of the clinker.
5. Grinding, and the addition of limestone and gypsum ($CaSO_4 \cdot 2H_2O$).

As mentioned, these are the general steps of what is called the Dry Method. The wet method is essentially the same process, but it involves the material being in a liquid slurry (America’s Cement Manufacturers, 2014).

As far as the reaction chemistry that causes cement ultimately to form as a solid, the material must first set, and then harden. Example reactions for these broad steps are shown in Figures 24.2 and 24.3.

$$3CaO \cdot Al_2O_3 + Ca(OH)_2 + 12\,H_2O \rightarrow 4\,CaO \cdot Al_2O_3 \cdot 13H_2O$$

and

$$(8+x)H_2O + (3CaO \cdot Al_2O_3)_2 \rightarrow 2\,CaO \cdot Al_2O_3 \cdot 8H_2O + 4CaO \cdot Al_2O_3 \cdot xH_2O$$

and

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 7\,H_2O \rightarrow 3\,CaO \cdot Al_2O_3 \cdot 6H_2O + CaO \cdot Fe_2O_3 \cdot H_2O$$

Fig. 24.2: Hydraulic cement setting.

While the reactants and products of these three reactions may appear somewhat complex, they are all examples of the formation of single or mixed oxide hydrates. The examples of reactions which illustrate hardening in hydraulic cement, in Figure 24.3, are similar.

$$(2CaO \cdot SiO_2)_2 + (x+1)H_2O \rightarrow Ca(OH)2 + 3CaO_2 \cdot SiO2 \cdot xH_2O$$

and

$$(3CaO \cdot SiO_2)_2 + (x+3)H_2O \rightarrow 3Ca(OH)_2 + 3\,CaO_2 \cdot SiO_2 \cdot xH_2O$$

Fig. 24.3: Hydraulic cement hardening.

Both of these reactions are further examples that illustrate the formation of sparingly soluble hydrates which essentially form a solid solution. All of these reactions depend upon water, and thus can occur in or under water. While formulations change based on the specific need, the materials used by Roman engineers to build the now ruined piers at Caesarea off the coast of Israel roughly two millennia ago are similar to modern mixtures.

24.2.2 Nonhydraulic cement chemistry

The driving force for the formation of cement in a nonhydraulic mixture is the reaction of the material with carbon dioxide. The reaction chemistry for this, in the simplified form, is shown in Figure 24.4.

$$CaCO_3 \rightarrow CaO + CO_2$$

and

$$CaO + H_2O \rightarrow Ca(OH)_2$$

and

$$CO_{2(g)} + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

Fig. 24.4: Nonhydraulic cement formation.

While these three reactions together may seem rather circular, in that calcium carbonate is an ultimate starting material as well as a product, all the steps in Figure 24.4 are necessary. In the first reaction, calcium oxide must be made, as it is not mined. Calcium carbonate has to be heated to approximately 850 °C to form the calcium oxide. Next, the addition of water to the calcium oxide forms what is still often called the slaked lime ($Ca(OH)_2$). Finally, the atmospheric carbon dioxide is required to provide a driving force whereby the slaked lime hardens as calcium carbonate.

24.2.3 Other types of cement

What is called “energetically modified cement” (EMC), a term coined in the 1990s, uses somewhat different starting materials than Portland cement, but still results in a cement material that can be used in applications traditionally filled by cement. Such cement is made using the following: blast furnace slag, possibly fly ash, volcanic ash, and usually some amount of Portland cement and sand. The latter two are used in smaller amounts than in established cement blends, and this becomes a use for slag and fly ash, materials that throughout history were often discarded as waste. As with other cements, formulations vary with specific applications.

At the EMC Cement website, the organization proclaims: “Compared to (Legacy) Portland Cement? Over a 90% Reduction in the Carbon Footprint and Energy Consumption! – that’s an annual saving of up to 2.4 billion tons CO_2 and 2.3 trillion KWh of energy... ” (EMC Cement, 2014). Although such statements do not specify how such numbers are derived, and are obviously trying to prove a point for the industry, they are made precisely because strides are being made to produce end materials with cement in a more environmental friendly manner than what has been done historically. The use of ECM is continuing to grow, but has not yet displaced other methods of cement production.

24.3 Uses

Industrially, cement is always used as a binder in construction materials. When mixed with stone and sand, it is more properly called concrete, the common building material. The breakdown of cement uses does vary somewhat by country, but the statistics from the Mineral Products Association, from Great Britain are representative of most uses (Mineral Products Association, 2014) and are as follows:

- Housing, 35.7%
- Private commercial, 22.2%
- Infrastructure, roads and bridges, 19.9%
- Industrial buildings, 10.9%
- Public nondomestic, 10.5%
- Other, 0.8%

24.4 Recycling

The general population does not consider cement or concrete a recyclable material, simply because the cement and concrete applications that are present in a home are usually walls and supporting structures. But concrete can be broken into small pieces and reused, often in some further construction application. In this way, cement can be recycled. The driver to do so, as opposed to simply using old cement and concrete as a form of fill dirt, is an economic one. In other words, if it is cost-effective to reuse cement, it can be done.

Another area in which the cement industry produces a significant amount of by-product, but in which it has invested considerable time and manpower in the recent past to seek reductions, is the production of CO_2, a well-known greenhouse gas. On average, carbon dioxide emissions into the atmosphere have been at or over 900 kg per ton of cement produced, at the turn of the millennium. But by the year 2009, emissions at newer plants had dropped to below 800 kg per ton (Mineral Products Association, 2014; Cembureau, 2014). While this number is still high, efforts are continuing to find ways to utilize or capture CO_2 as it is generated.

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25 Asphalt

Asphalt still has the older name “bitumen” attached to it and can also be called “tar,” depending on the circumstances in which it is used and the source materials. Recovered from the heaviest fraction of crude oil, the viscous substance used in making roadways is a mixture of heavy hydrocarbons, and when mixed with stone becomes essentially a hydrocarbon-based concrete. Asphalt is used predominantly in road construction, and to a lesser extent as a waterproofing material, often for commercial or residential buildings.

The United States Geological Survey Mineral Commodity Summaries does not track asphalt, but it does track sand and gravel as a category, as well as crushed stone (US Geological Survey, 2014). Both are plentiful and widespread, and both can be mixed with asphalt as it is being prepared for use.

25.1 Source material

In almost all cases, the source material for asphalt is the heaviest fraction of crude oil, the fraction that cannot be broken into some smaller hydrocarbon even at elevated temperature and used either as a feedstock for some plastic or as a motor fuel or motor fuel additive. Thus, asphalt production is tied to crude oil refining.

When used as a road material, asphalt is more properly called asphalt concrete, because it is mixed with stone, and can comprise more than 90% stone and other additive material. Asphalt serves to bind the other aggregates together.

25.2 Formulations and production

Formulas for asphalt are difficult to write and represent in terms of traditional Lewis structures or molecular formulas, because it is a complex mixture of heavy hydrocarbons and multiple fused polycyclic hydrocarbons. Also, since asphalt can be so viscous that it does not flow, it can be mixed with other materials – usually lighter, liquid hydrocarbons – to make the end product easier to use and apply. However, this also makes the mixture more complex. In all cases except what is called “cold patch,” asphalt is heated prior to use. When asphalt must be transported long distances and kept hot for the entire transport, trucks are sometimes used that have the hot exhaust gases from the engine evacuated through tubes which help keep asphalt in a state where it can be worked upon arrival at its destination.

25.3 Uses

Close to 90% of asphalt is used for road construction. Other materials that compete with it for this use are stone, brick, and interlocking paving brick, each of which is not made with a hydrocarbon source as a starting material.

Asphalt is used to a lesser extent for waterproofing building roofs. Generally, commercial or corporate buildings that have large, flat roofs are waterproofed in this way, but some residential housing is as well. Asphalt shingles are used on houses in large parts of the world, but compete with several other different types of roofing material, such as ceramic tiles.

The difference in asphalt when used in road construction versus roofing water proofing is often a difference in what additives are mixed with the starting material. As mentioned, asphalt is often so thick that it does not flow, and thus some lighter hydrocarbon is mixed with it to lower its viscosity. Kerosene has been used in the past, but it is being displaced by other liquids that are considered environmentally more benign. This is driven by the fact that when road material is put in place, the kerosene simply evaporates into the surrounding atmosphere.

A smaller use for asphalt than these two is inks and paints. Paints and inks made with asphalt tend to have high resistance to weathering, and are thus used in outdoor applications.

25.4 Reuse and recycling

When it comes to recycling of commodities, most individuals think in terms of paper, plastic, glass, or aluminum. These are definitely the products recycled from residences the most. But asphalt is routinely recycled when a road or parking area is resurfaced. Indeed, the National Asphalt Pavement Association refers to asphalt as, “the #1 recycled product in America” (National Asphalt Pavement Association, 2014). Both the Association of Modified Asphalt Pavers and the Asphalt Institute also point out the re-cyclability of asphalt (Association of Modified Asphalt Producers, 2014; The Asphalt Institute, 2014). In general, the only time asphalt is disposed of in a landfill is when the area being dug up could no longer be used as a road or a paved surface. Even in such cases, if other construction projects requiring asphalt are underway nearby, it can simply be trucked to the new site and used there.

Bioasphalt

A relatively new term in the lexicon, “bioasphalt,” means asphalt produced from some renewable, nonpetroleum-based source. The advantages in using bioasphalt are rather obvious, that no petroleum is consumed in its production, and that carbon-based material which might otherwise be unused, and disposed of in landfills, is utilized in making it. True bioasphalt can be made from a wide variety of natural sources, such as corn, molasses, potato starch, or sugarcane residues. Some firms have already begun marketing bioasphalt, but have chosen to keep their formulas proprietary. Usually such firms promote the material in terms of its environmental friendliness. For example, Avello Bioenergy states at its website: “Bioasphalt binder is produced from domestic nonfood resources such as agricultural and wood residues. Using biomass derived Bioasphalt binder decreases our national demand for imported petroleum” (Avello Bioenergy, 2014).

Also, a material can be called bioasphalt when it is made from once-used engine oils, although this is more properly asphalt that has been made from a petroleum base, but used once prior to its conversion to asphalt.

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26 Biofuels and bioplastics

A significant amount of studies have been about biosources of motor fuels (Demibras, 2008; Aresta et al., 2012; Olssen, 2007; Brown and Brown, 2012; Drapcho et al., 2008; Biomass Magazine, 2014; Ethanol Producer Magazine, 2014), and a somewhat smaller number of studies have been carried out concerning the use of biosources to produce chemicals that in turn are used to produce plastics (Pilla, 2011). In both cases, despite a large amount of what can be called proof-of-concept studies, only a few materials have been advanced to the point where they are made into biofuels or bioplastics on an industrial scale. Bioethanol is one such fuel. It is almost always made from corn in the United States and sugar cane in Brazil (sugarcane.org, 2014), the two largest national producers of bioethanol. Biodiesel is another, produced mainly from soybeans in Brazil. Plastic from starch is one polymer product that is now an industrial-scale production. Additionally, polylactic acid from biosources is another plastic that can now be made on a large scale from renewable material.

The ability of biosource material to replace petroleum continues to be the subject of heated debate, with production costs, necessary quantities, and the cost of related secondary materials and processes factoring into the debate (Advanced Biofuels Association, 2013; Renewable Fuels Association, 2014; Oil Seed Crops Food and Energy, 2014). Proponents point out the environmental benefits of using renewable materials – as opposed to fossil, petrochemical material sources – for producing fuel and plastics. Detractors point out that fertilizer used for crops such as corn is made from fossil sources. Organizations such as the Renewable Fuels Association indicate that biofuels are more about the economic health of rural communities in the United States than about the environment when they state in their literature, “. . . the ethanol industry continues to have a profoundly positive impact on the fiscal health of rural America” (Renewable Fuels Association, 2014).

26.1 Corn for bioethanol

Undoubtedly, a great deal of effort has been put into converting corn into ethanol for use as a motor fuel. In the United States, fuel blends are in the process of changing from what is called E5 – meaning 5% ethanol in a traditional gasoline blend – to E10. Most fueling stations in the United States have been using E5 gasoline blends for several years (Renewable Fuels Association, 2014; National Corn Growers Association, 2014; American Coalition for Ethanol, 2013). Some stations also offer E85 – which is 85% ethanol – for use in automobiles equipped with engines that are designed to combust this fuel.

The reaction chemistry by which corn is converted into ethanol is shown here in a simplified form in Figure 26.1, utilizing $C_6H_{12}O_6$ as a representation for the starch component in corn (which is also used in numerous discussions of this type as a single glucose molecule).

$$C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH_{(l)} + 2\,CO_{2(g)}$$

Fig. 26.1: Ethanol production from corn starch.

Water is absolutely required for this reaction, a fermentation, to occur, but is not shown in the reaction since equi-molar amounts are used and produced. The above reaction can represent any fermentation in which a starch is broken down into ethanol, and indeed, this reaction is a simplified version of that which represents the production of beer or wine. Sources for this fermentation include every plant material that produces sufficient starch, such as corn, sugarcane, fruits, sugar beets, or even wheat and rice. What is sometimes missing from the discussion about ethanol production is the co-production of two moles of carbon dioxide for every starch unit utilized. Critics claim that the co-production of the CO_2 contributes to the production of greenhouse gas accumulation, while proponents claim that this CO_2 will be reutilized in the production of further crops, and thus is not a net contributor.

26.2 Sugar cane for bioethanol

While bioethanol is routinely made from corn in the United States, in other parts of the world – generally warmer ones – sugarcane is grown easily and can be used as the feedstock for ethanol. Brazil has been producing ethanol from sugarcane for decades, where there is sufficiently warm climate for much of the year, as well as enough arable land on which to cultivate it.

The arguments made about bioethanol production from corn are generally the same as those made when discussing bioethanol from sugarcane. Recently, Shell Oil has formed a collaboration with the Brazilian firm Cosan for this type of fuel production, and states at its website: “This biofuel can reduce CO_2 emissions by around 70% compared to standard petrol” (Shell, 2014). Perhaps obviously, detractors will point out that the production of such biofuel comes at a cost of claiming usable land from parts of what had been the Amazon rainforest.

26.3 Soybeans for biodiesel

Diesel is the other major motor fuel produced from some plant material. In the recent past, the term biodiesel has been coined to differentiate between this and the traditional fuel, which is now often called petro–diesel or mineral diesel. As a product, biodiesel is now made on such a large scale that trade organizations exist which are wholly or in part dedicated to its promotion and use (Biomass Magazine, 2014; Biodiesel Magazine, 2014).

Soybeans have become a major plant source for the production of diesel fuel, although biodiesel can also be produced from other plants as well as waste animal fats. The

United States Department of Agriculture GAIN Report from 2012 states, “Biodiesel is a trans-esterified vegetable oil also known as fatty acid methyl ester produced from soy oil, rapeseed oil, other vegetable oils, animal fats, and recycled cooking oils” (USDA, 2014). It is these fatty acid methyl esters, often abbreviated FAME, that are the biodiesel, although methanol is not the only alcohol that can be used productively in the trans-esterification. The glycerin that is co-produced is not used as fuel.

Because the plant and animal sources do not have a common starting molecule –like starch for bioethanol production – there will be some variety in the materials that ultimately become biodiesel. In general though, fats or oils are trans-esterified in a reaction that breaks down tri-acyl-glycerides into 3 moles of esters, and a mole of glycerin. The three esters may or may not all be the same, depending on the starting material. A simplified version of this reaction is shown in Figure 26.2.

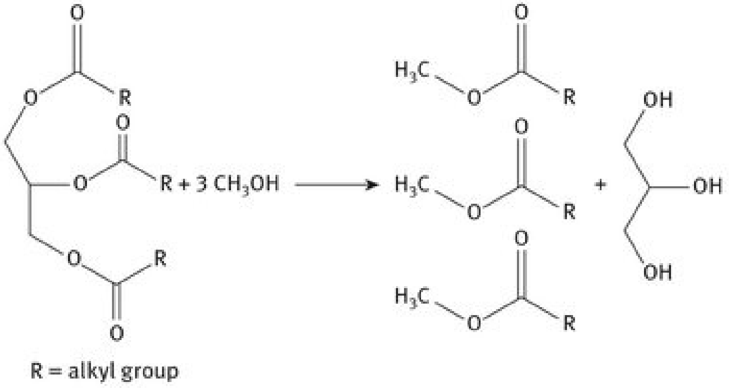

Fig. 26.2: Biodiesel production.

As mentioned, animal sources, usually waste fat from some meat production facility, can be used to produce biodiesel as well. Several poultry processing companies achieved a certain amount of fame in 2007 in the popular press by entering into agreements with diesel producers to use their excess chicken fat for biodiesel. Such waste fat had normally been used in soaps and cosmetics (Washington Post, 2014). These animal-derived sources will produce different fatty esters than plant sources. Examples of two common FAMEs produced in this manner are shown in Figure 26.3.

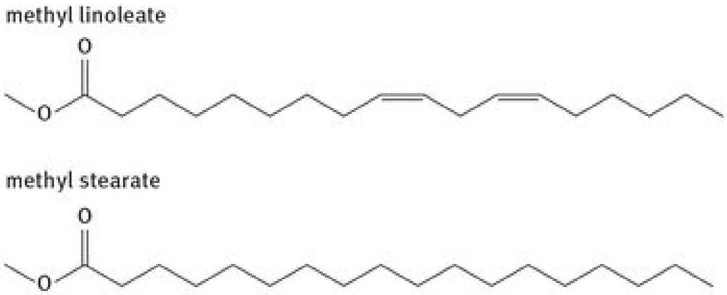

Fig. 26.3: Example fatty acid methyl esters.

26.4 Algae as a fuel source

It may seem odd to consider algae as a viable source for biofuels, but some species of algae are capable of the production of significant amounts of material that can be transformed into biodiesel (National Renewable Energy Laboratory, 2014; Sustainable Development of Algal Biofuels, 2014). These species are capable of producing up to 50% oil based on their weight, and thus there is considerable interest in scaling such production up to an industrial level. Additionally, the possibility exists of using the algal material that does not become biodiesel for the further production of bioethanol. This has been studied rather extensively by the National Renewable Energy Laboratory (NREL) and small-scale production has been proven to be feasible. However, this has not yet progressed to an industrial scale operation (National Renewable Energy Laboratory, 2014).

26.5 Cellulosic bioethanol

A debate continues on the use of corn, sugarcane, soybeans, and other food crops for biofuels, precisely because these crops are staple foods, and the world still has over 1 billion people living in some state of malnourishment. In part because of this, and in part because of the potential market for biofuels from all sources, a great deal of energy has been put into the production of what is called cellulosic ethanol, meaning ethanol produced from biomaterial that is cellulose based as opposed to starch based. This includes corn stover, bagasse, switch grass, and other nonfood plants (Biomass Magazine, 2014; Advanced Biofuels Association, 2013; National Corn Growers Association, 2014).

These sources of bioethanol are collectively referred to as second generation biofuel materials. While several companies are close to starting up cellulosic bioethanol production facilities, all with enzymes that are proprietary, only INEOS Bio had opened a plant at Vero Beach, Florida by the end of 2013 (Renewable Fuels Association, 2014). If the production costs for such operations can be lowered enough, the use of cellulosic ethanol could significantly alter what fuels are offered for automotive use.

Fig. 26.4: Drinking cup made from biodegradable materials.

26.6 Production of bioplastics

More than fuel can be made from bio-based materials. Research has been done for at least the last 30 years on the production of plastics from bio-based sources, with the twin aims being the production of materials from entirely renewable sources and biodegradable plastic materials for consumer use (Corbion Purac, 2014).

The second aim would in theory eliminate the problem of nonbiodegradable plastic materials ending up in landfills. In the recent past, BASF marketed material for waste bags that were manufactured precisely to be biodegradable, but found that sales to consumers ended up being low, which may be a result of the finished product's appearance or feel (BASF, 2014). In general, it appears that the ecological compatibility and friendliness of such products need to be advertised heavily, as shown in Figure 26.4, two views of a disposable drinking cup made from renewable materials.

26.6.1 Bio-polylactic acid

Polylactic acid (PLA), has recently been brought to market from biofeedstock. Both corn starch and sugarcane starch have been used to produce lactic acid. Several companies that produce it do so while advertising the environmental friendliness of the material. For example, Thyssen–Krupp states at their website: "T-shirts, coffee cups, fast food packaging, bottles and other everyday items: Biobased plastics, also referred to as polylactic acids (PLA), can be used to make a wide variety of products –in environment-and resource-friendly processes" (Thyssen–Krupp, 2014).

The polymerization of the starting material proceeds as is shown in Figure 26.5.

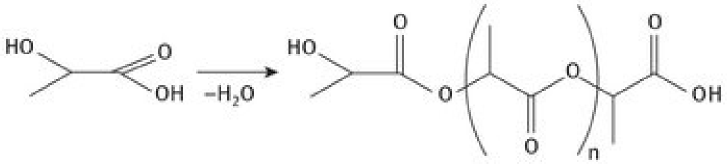

Fig. 26.5: Polylactic acid production.

26.6.2 Bio-poly-starch

Producing polymers from starch actually has a fairly developed history. Starch can be obtained from plant sources, and processed into what is generally called thermoplastic starch. BASF has had success with what it labels Ecoflex®, a starch–polyester blend that biodegrades in only a few weeks (Corbion Purac, 2014).

Such polymers find use in applications as different as packaging "peanuts" and thin films for food storage and preservation. Whether or not their production is profitable and continues to be connected indirectly to the price of crude oil, from which plastic monomers, and ultimately many plastics, are derived.

26.7 Recycling and reuse

Fuels are very seldom recycled, and thus there are no plans for the recycling of biofuels. However, the production of bioplastics is often aimed at producing a plastic material that biodegrades, and thus does not need to be recycled. The fact that a plastic material has been made from biosources as opposed to petroleum sources does not automatically mean that it will be biodegradable, however. In such cases, bioplastics are generally recycled in the same secondary use streams as the petroleum-based plastics. The resin identification codes (RIC codes) 1–7 found on most plastic consumer use products, such as bottles, plates, cups, and plastic cutlery, can be applied to plastics made from biosources as well. This recycling can be a national program, as in some European Union nations, or can be left to smaller governmental bodies, as with the individual states within the United States.

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