

History of Food Packaging

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Introduction

The historical development of food packaging, together with an appreciation of the origins of packaging materials and knowledge of the pioneering efforts in food package development, can be both instructive and inspirational, particularly to students of food packaging and those working in the area of food package design and development. The highly sophisticated food packaging industry which supplies modern society today is far removed from the simple packaging activities of earlier times (Goddard, 2000).

During nomadic times in human history, people would eat what they could find and collect in the surrounding environment, without worrying about protecting and storing their food. However, when humans started to settle in communities, the need to contain and store food became essential, as did the need for suitable ways of preserving and packaging food.

A detailed description of the early period of packaging from 10,000 BCE until the beginning of the first Industrial Revolution in 1760 is given by Sacharow and Brody (1987). Glass vessels dating back to 3000 BCE have been discovered, together with pottery vessels that date from even earlier times; both were used for food storage and sealed with beeswax, pitch or cork. Leather bags for wine and milk, as well as wooden barrels coated on the inside with pine resin, were in use in the 1st century CE.

The first Industrial Revolution heralded the transition to new manufacturing processes in Europe and the US in the period from about 1760 to sometime between 1820 and 1840. This led to improvements in the manufacture of wood, paper, metal, and glass and facilitated the use of these materials in food packaging and preservation. The 20th century saw major improvements in rigid and flexible packaging materials. In the 1950s, new plastic materials were introduced and used in packaging films. From the mid-20th century there have been a number of major packaging developments that have shaped the modern packaging and food preservation world. Examples include aseptic processing and packaging, modified atmosphere packaging, microwavable packaging, and smart, active and intelligent packaging systems.

This article discusses the history of food packaging from the early 19th century until today with an emphasis on the inventors and materials that have contributed to today's vibrant food packaging industry. It highlights the rationale, technology path, hard work, and sophistication behind the many different packages consumers use today. It also demonstrates the determination, persistence and tenacity required by inventors to successfully commercialize their ideas. A salutary note for today's inventors is the fact that Nicolas Appert, Louis-Nicolas Robert and the Fourdrinier brothers died in poverty while their inventions live on to the present day.

Glass Containers

Glass has been defined as "an amorphous, inorganic product of fusion that has been cooled to a rigid condition without crystallizing." Although glass is often regarded as a synthetic material, it was formed naturally from common elements in the earth's crust long before the world was inhabited. Natural materials such as obsidian (from magma or molten igneous rock) and tektites (from meteors) have compositions and properties similar to those of synthetic glass; pumice is a naturally occurring foam glass.

Although the origin of the first synthetic glasses is lost in antiquity and legend, the first glass vessels were probably sculpted from solid blocks about 3000 BCE. In about 1000 BCE, the techniques of pouring molten glass or winding glass threads over a sand mold were developed, resulting in the formation of crude but useful glass objects. However, the real revolution in glassmaking came around 200 BCE with the introduction of the blowing iron, a tube to which red-hot, highly malleable glass adheres. Blowing through one end of the iron causes the viscous liquid to balloon at the other end, leading to the production of hollow glass objects. By CE 200, articles of glass were in fairly common use in Roman households. During the following 1000 years, glassmaking techniques spread over Europe. However, up until the mid-19th century glass remained expensive as bottle and glass making followed virtually the same craft-based processes that had been used for many centuries. It was not until improved techniques in the mid-19th century brought down the price of bottles and jars to a relatively affordable level.

The first known patent for pressing glass by mechanical means was granted to John P. Bakewell in 1825 to make pressed glass knobs for furniture. Pressed glass involved mechanically pressing the molten glass into a plain or engraved mold by means of a plunger, enabling glassmakers to spread the thick, molten glass quickly throughout the mold before it solidified. This invention quickly led to the mass production of glassware and greatly reduced its cost. The pressing process became the single most important

factor in making glassware affordable for everyday use. Pressed glass was also produced in England with the first pressing machine being installed at Stourbridge by W.H.P. Richardson in 1833. From there pressed-glass technology spread to other parts of England and continental Europe as well. Good quality flint glass was used exclusively until the mid-1860s, when a cheaper but more breakable soda-lime glass was introduced.

Glassmakers had tried without success to mechanize glassblowing by imitating the method for making bottles by hand where a bottle's neck and finish (mouth) was the final step. The first patent for a bottle-making machine was issued in 1859, and several others were patented in the following two decades. None of these devices proved successful in practice and the development of machine-made glass bottles only became possible when it was recognized that the finish had to be formed first rather than last. Two American patents, Gillender's in 1865 (US 51386) and the Atterbury brothers in 1873 (US 140,236), both described molding processes where the finish was formed as the first part of the machine blowing operation. The brothers James S. and Thomas B. Atterbury, proprietors of the Atterbury & Co. glass factory in Pittsburgh, Pennsylvania took out a total of 110 patents between 1862 and 1897: 79 for manufacturing improvements and 31 for designs.

The same press-and-blow method was patented in 1882 by American glassmaker Philip Arbogast from Pittsburgh (US 260,819) in 1882 for an approach that first pressed a blank in a mold and then transferred it to a blowing mold for its final shape, later referred to as a "press-and-blow" process. In 1884, Daniel C. Ripley, Jr., a friend of Arbogast, began to experiment with this machine, or an adaptation thereof, and in 1885 purchased the patent rights for \$450 as a friendly gesture. The Ripley Company was taken over by the United States Glass Company, which then granted manufacturing licenses. The Arbogast process was particularly suited for wide-mouth as well as thick-walled jars. Although these machines started the glass industry on the road to mechanization, they still needed to have hot glass fed into their molds by hand. Use of machines was limited by strong glass blowers' unions. The Arbogast machine did not enter large scale production until 1893 when it was used by Enterprise Glass Company, a non-union shop, to make vaseline jars (Cable, 1999), and later, fruit and other jars as well (Meigh, 1960). The H.J. Heinz Company, a major user of jars and wide-mouth bottles, used the Arbogast process. Henry Heinz had been an innovator in glass packaging as early as the 1870s and glass bottles were the key to his success as he realized that the package was as important as the product (Skrabec, 2011).

The plunger employed in the press-and-blow process, however, was too large to be used on narrow-mouthed containers. The first machine to make narrow-mouthed bottles was patented in 1886 by Howard Matravers Ashley, of Ferrybridge, England (US patents 403,023 and 416,149 issued in 1889). This was the first blow-and-blow machine and was one of the first of the semi-automatics although it still required a large number of workers to operate. Despite attracting considerable interest in France and Germany during the 1890s, it was not commercially successful. The first satisfactory semi-automatic machine for making narrow-mouthed bottles was not constructed until 1908. However, fully automatic machines were coming into use by this time, and the semi-automatic progressively declined in popularity, until in 1919 there were only ten such machines in use (Scoville, 1948).

For the rest of Europe, the history of the transition to machine-made glass is sketchier. Germany had the largest glass container production in Europe prior to the introduction of the Owens machine (see below) and was the major shareholder in the E.V. cartel formed in 1907 to purchase European rights to the Owens machine to limit its production to 10 per cent of the glass containers for the year of introduction with 5 per cent increases for the following two years. Before the Owens machine came on the scene, a very successful device known as the Schiller Semi-Automatic, a press-and-blow machine, was put into commercial use in Germany in 1906. Between 1906 and 1932, 1150 Schiller Semi-Automatic bottle-making machines were installed throughout Europe, 223 of them in Germany itself (Schulz et al., 2016).

While the 1890s was a period of revolution in glass technology, the new technology did not begin to reduce the number of hand glass blowers until after 1905, because expanding demand for glass containers accommodated both the new technology and the old.

Edward Drummond Libbey opened the Libbey Glass Co. in Toledo, Ohio, in 1888, sponsoring a demonstration plant at the Chicago exposition of 1893 (Skrabec, 2011). His success depended heavily on the self-taught inventor Michael Joseph Owens who started his career in a glass factory in Wheeling, WV at the age of 10. Owens filed for a patent on his "machine number one" in December 1899 and it was accepted in May 1904 (US patent 774,691). Several German patents claimed prior inventions, but the US patent went to Owens. Years later, once Owens was confident about commercialization, Toledo Glass bought up the rights to these German patents to avoid litigation (Skrabec, 2007). None of these German patents was ever demonstrated as practicable. The machine was a major advance over the semi-automatic machines. This masterpiece of automation preceded Henry Ford's celebrated introduction of an automobile assembly line by a full decade and further reduced the role of the skilled craftsmanship of the glass blowers (Shackelford and Shackelford, 2018). In 1983 the American Society of Mechanical Engineers designated the Owens Automatic "AR" Bottle Machine developed in 1912 as the 13th International Historic Mechanical Engineering Landmark. He was inducted into the National Inventors Hall of Fame in 2007. Owens eventually held 45 US patents, either independently or jointly with others (Fig. 1).

In 1903 The Owens Bottle Machine Company was incorporated with a capital of \$3,000,000 to license rights to the machine to various glass companies for the production of specific types of bottles. By 1909 three other companies had taken up licenses to use the machine and had put 46 machines into production (Scoville, 1948). Their success with the machine and further improvements by Owens increased the number of glass companies taking out licenses. Owens next convinced the company to move beyond licensing and their small demonstration plant, and in 1909 they began to build their own bottle factories (Twede, 2012). The spread of the Owens Bottle Machine to other countries was fairly rapid. In 1906 a license was issued to the Canadian Glass Manufacturing Company for a glass works and by 1914 there were 60 Owens machines in Europe (Miller and Sullivan, 1984).



Figure 1 Some common glass bottle shapes that have become closely associated with particular beverages such as wine, beer and milk. Designed by macrovector/Freepik.

In 1929 the Owens Bottle Machine Company merged with the Illinois Glass Company to form Owens-Illinois, and in 1935 Owens-Illinois bought Libbey Glass for \$5 million. It changed its name to O-I in 2005 and today is a Fortune 500 company and the largest manufacturer of glass containers in North America, South America, Asia-Pacific and Europe. Approximately one of every two glass containers made worldwide is made by O-I, its affiliates, or its licensees (<https://en.wikipedia.org/wiki/Owens-Illinois>).

Added impetus was given to automatic production processes in 1923 with the development of the gob (mass or lump of molten glass) feeder, which ensured the rapid supply of more consistently sized gobs in bottle production. Soon afterward, in 1924, Henry W. Ingle of the Hartford Empire Company, Hartford, Connecticut, applied for a patent (US 1,843,159 granted in 1932) for the IS (now generally taken to mean 'individual section' but actually named after its inventor Henry Ingle and the company President Charles Goodwin Smith) blow and blow (B&B) machine (Hanlon et al., 1998). Used in conjunction with the gob feeders, IS machines allowed the simultaneous production of a number of bottles from one piece of equipment. The gob feeder-IS machine combination remains the basis of most automatic glass container production today.

Further developments have occurred, resulting in the production of a wide range of glass containers for packaging. The two main types of glass container used in food packaging are bottles (which have narrow necks) and jars (which have wide openings). About 75% of all glass food containers in the US are bottles and approximately 85% of container glass is clear, the remainder being mainly amber. Generally, today's glass containers are lighter but stronger than their predecessors, with the weight of many bottles and jars having been reduced by 25%–50% over the last 50 years. Through developments such as this, the glass container has remained competitive and continues to play a significant but declining role in the packaging of foods.

One of the major advantages of glass as a packaging material is its capability to be formed into a wide range of shapes related to specific end uses, customer requirements and aesthetic appeal. The commercialization of computer-aided design (CAD) and computer-aided manufacture (CAM) has made the task of designing and manufacturing new glass containers considerably easier and more rapid. This has led to greater flexibility and resulted in considerable efficiencies through a more thorough analysis of stresses and strength/weight factors and calculation of likely mechanical performance. In particular, the application of finite element analysis (FEA) has resulted in significant lightweighting of glass containers with improved mechanical performance (Robertson, 2013).

The most important property of glass containers is their inertness: virtually nothing migrates from, to or through glass, and glass contains no foreign odor or flavor. Furthermore, glass does not react with the environment, corrode, oxidize or otherwise deteriorate (Sacharow and Brody, 1987). For these reasons, glass containers remain the benchmark for food packaging, with their transparency often seen as a plus by consumers. Although glass has great compressive strength, it breaks under tensile load, almost exclusively in areas under tension attributable to deformation that creates bending stresses.

Closures

Historical Development

Bottles and jars require closures and development of cost-effective, consumer-friendly closures has occupied inventive minds for at least the last 200 years. Bail closures on bottles containing carbonated beverages were invented by Henry William Putnam from Cleveland, Ohio in 1859 (US patent 23,263). These involved heavy wire bail attached to a bottle's neck that swung over the cork to hold it in. In 1872, English mechanical engineer Hiram Codd patented a bottle filled under gas pressure which pushed a marble against a rubber washer in the neck, creating a perfect seal; it became known as the Codd bottle. The Codd-neck bottle

was designed and manufactured with thick glass to withstand internal pressure, and a chamber to enclose a marble and a rubber washer in the neck. Mineral water soda manufacturers who wanted to use Codd's Globe Stopper bottles had to pay a yearly fee for a license to use his patent bottle. Codd's patented globe stopper bottles have been manufactured by the Khandelwal glass works in Uttar Pradesh, India since 1981. His earlier bottles are prized by antique bottle collectors worldwide, but few have survived as children could not resist breaking the bottles to recover the marbles.

The Chase cap has gained fame through its association with the Mason jar, patented in 1858 by John L. Mason (US patent 22,186) with Chase's patent very much in mind. Chase's cap was in continuous production for well over a century, helped along by the addition of glass and porcelain liners patented in 1869 by Lewis R. Boyd (US patent 88,439). With such vitreous liners the screw cap also became available as a screw band. Caps of Chase's design are occasionally found made of aluminum, almost certainly a 20th century variation (Bender, 2016).

A flip-top, swing-top, or Quillfeldt stopper was patented by Charles de Quillfeldt from New York in 1875 (US patent 158,406) and was used for bottles containing carbonated beverages such as beer or mineral water. The mouth of the bottle was sealed by a stopper, usually made of porcelain, fitted with a rubber gasket and held in place by a set of wires. The bottle could be opened and resealed repeatedly without the use of a bottle opener. The flip-top was the dominant method of sealing beer and mineral water bottles prior to the invention of the crown cork and is still used today to a limited extent (Fig. 2).

Shortly after patenting the design, de Quillfeldt sold the patent rights to several individuals, including Henry W. Putnam from Bennington, Vermont who adapted the design for use as a stopper on fruit jars and received a patent in 1882 (US patent 256,857). The jars he produced were embossed "Trademark Lightning" on the side with "Putnam" on the base and gave the generic name "Lightning" to jars that used this closure after Putnam's rights expired. Karl Hutter from New York secured the patent rights for beverage bottles. Hutter received a patent (US patent 56,225) in 1896 for an improved 'double-seal' stopper that contained a minimum of elastic material and required a minimum amount of pressure to seat it in the bottle. This stopper revolutionized beer bottling and was an almost instant success. There were many imitators of this patent over the years, but they all worked on the same principle of sealing the mouth of a bottle with a swing-away, multiple-use, rubber gasket. Innovative printing technology in the very late 19th century allowed brewers and bottlers to have their company name, address, and a logo or monogram imprinted on top of this Hutter stopper. This stopper was eventually replaced with the crown cork closure.

The traditional pressure-retaining closure has been the crown cork, a crimp-on/pry-off friction fitting closure made from tinplate with a fluted skirt (angled at 15° to maintain an efficient seal) and a cork or plastisol liner. The crown cork was patented in 1892 (US patent 468,226) by William Painter from Baltimore, Maryland, who said of his invention (so it is claimed) "this closure gives a crowning and beautiful effect to the bottle" and the name crown stuck. It was simple in concept, economical to produce and provided a friction-fit sufficient to seal pressurized beverages. The flared cap skirt, in conjunction with the smoothness of the bottle neck, provides easy access through the prying motion of a bottle opener. The crown cap was not an immediate success since it required new bottles, new bottling machinery, and a level of uniformity of bottle manufacture that was just beginning to be possible in the early 20th century. The crown cork of today is still much the same, except that the teeth on the skirt have been reduced from 24 to 21, ECCS is used rather than tinplate, and PVC plastisol or some type of olefinic material linings have largely replaced cork (Pitman, 1999). A relatively recent improvement has been the introduction of twist-off crown corks applied to a 26 mm twist finish that can be removed by hand.

Painter founded the Crown Cork & Seal Company of Baltimore in 1892 and by the time he died in 1906, Crown has greatly expanded its manufacturing base to include Europe, South America and the Asia Pacific. In 1968 Crown developed the first all-plastic closure for carbonated soft drinks, and in 1990 they acquired major portions of former industry leader Continental Can Company. Global Closure Systems is a privately-owned French company created as a result of the purchase in 2005 by PAI Partners, a French private equity firm, of the closures business previously operated by Crown Holdings Inc.



Figure 2 Unopened swing top beer bottle closure https://commons.wikimedia.org/wiki/File:Swing_top_beer_bottle_closure,_unopened_.jpg#filelinks and a Codd bottle.

Screw Caps

Screw caps were originally an internal thread design. A glass bottle or jar with an internal screw-thread immediately below a beveled gasket-seat was patented in 1872 (US patent 130,208) by Himan Frank of William Frank & Sons, Inc. of Pittsburgh, PA. A stopper suitable for use with the bottle or jar mouth had a threaded end, and a gasket with overhanging top.

The first screw cap of a standard design to be widely used in the US was patented in 1857 by John K. Chase of New York City (US patent 18,498). These caps were made of zinc, with deep screws, shallow threading, and raw distal edges. The advantage of using zinc was that it was elastic enough to make allowances for the hand-tooled screw finishes of the time. The improvements patented by Chase included forming the caps by spinning zinc discs over a screw finish template to avoid the problems inherent to soldered seams (Bender, 2016).

The 1920s saw the development of molded plastic screw caps made from phenolic resinoids. By 1930–31, molded urea-formaldehyde resinoids allowed screw caps of lighter weight construction and softer, lighter colors (Bender, 2016).

Lug Closures

Twist-off metal lug closures, which require less than one turn to apply and remove, were developed in the US in the early 1950s, a patent (US patent 2,841,304) being awarded to Donald H. Zipper and assigned to White Cap Company, Chicago, Illinois in 1955. They are often referred to as 'White' caps. The closures have lugs or protrusions on the inner edge that engage with an interrupted thread on the container neck. In 1956 White Cap became a subsidiary of the Continental Can Company.

Roll-On Tamper-Evident (ROTE)

A ROTE aluminum screw cap was first introduced in 1924 by the Aluminum Seal Co. as a closure on bottles of prescription drugs. It is now used where critical sealing requirements such as carbonation retention, vacuum retention and hermetic sealing are to be met. The closure is produced as an unthreaded shell containing a liner and is applied to the finish on a plastic or glass container. A thread is formed in the closure matching the bottle thread. This ensures a tight fit even though there may be defects in the container finish.

Cork

Cork as a stopper for vessels goes back to antiquity, being mentioned for such use by the Greek author Pliny the Elder during the 1st century CE. Cork comes from the bark of the cork oak tree (*Quercus suber*), native to southwest Europe and northwest Africa, and is grown commercially for its cork mainly in Portugal and Spain. The cork stopper has been used as a closure on glass bottles for over 25 centuries and provides an incomparable friction-hold seal. With a high cellular density, cork is compressible, elastic, largely impervious to air and water and low in thermal conductivity. However, some wines sealed with natural cork suffer from "cork taint", an objectionable taint caused by TCA (2,4,6-trichloroanisole) and other organohalogens that have taste thresholds in the parts per trillion range. Various approaches have been adopted to overcome the problems of cork taint in wine and provide the impetus for alternative closures (Goode, 2010).

A challenge to the cork was the development in France in the late 1960s of an aluminum rolled-on closure known as STELVIN®. Research suggested that it performed better than the bark cork. The STELVIN® closure is made up of a screw cap, a long printable skirt and a liner specifically designed for contact with wine. The wad or liner consists of three or four components depending on the anticipated shelf life of the wine. The very first STELVIN® aluminum closure (originally named STELCAP VIN) was developed by the French company Le Bouchage Mécanique in Chalon-sur-Saône, Burgundy, France in 1964 and the brand was officially registered in 1976. At the time, the STELVIN® closure was deemed to be the ideal closure for Chasselas, a Swiss white wine that was particularly subject to cork taint. Now part of the Amcor group, the STELVIN® closure continues to replace corks, especially in New World wines. In 2013, Amcor, the manufacturers of STELVIN®, launched four new liners with different OTRs.

Diam, made by Oeneo Bouchage, is an in-neck closure made up of small granules of cork that have been cleaned with supercritical CO₂ for selective extraction of volatile compounds from cork and combined with synthetic microspheres. Using a process originally developed in the 1950s by Maxwell House to decaffeinate coffee, the Diamant® supercritical CO₂ patent further developed that technology specifically for corks, the first work being initiated in 1997 and patented in 2002 (European patent 1,216,123). They also offer different OTRs with the Diam 30 released in 2014 developed for long bottle aging of grand cru style wines with the mechanical properties of the cork being guaranteed for 30 years.

Cellulose

According to Röper (2002), Nature produces 170 billion metric tonnes per year of biomass by photosynthesis, but only 3.5% is used by humans for food and nonfood purposes. However, the vast majority of the remaining 96.5% is not available for industrial use, either because it is an intricate part of the local ecosystem, or because it resides in areas where its collection is unpractical. Biomass

carbohydrates account for 75% of this biomass and are the most abundant renewable resources available; they are currently viewed as a feedstock for the so-called “green” chemistry of the future including biobased plastics.

Vegetable biomass is generated from CO₂ and H₂O using sunlight as the energy source, producing O₂ as a by-product. The primary products formed are hexoses (six-carbon sugars), of which glucose is the most common, and pentoses (five-carbon sugars), of which xylose is most common (Corma et al., 2007). Cellulose is formed by polymerization of glucose and hemicellulose is a polymer of glucose and xylose. There is a third component, lignin, that is a highly cross-linked polymer built of substituted phenols and, together with cellulose and hemicellulose, gives strength to plants.

Cellulose, a complex carbohydrate consisting of 3000 or more D-glucose units (anhydroglucose unit) is the basic structural component of plant cell walls and comprises about 33% of all vegetable matter (90% of cotton and 40%–50% of wood is cellulose). It is the most abundant of all naturally occurring organic compounds and was first described in 1838 by the French chemist Anselme Payen who also isolated the enzyme diastase (amylase) from malt.

Cellulose is mainly used to produce paperboard and paper packaging. Numerous cellulose derivatives can be produced by the dissolution of normally insoluble cellulose, through the replacement of the hydroxyl groups with different radicals and their reclamation from solution to produce films for packaging such as cellophane. Cellulose for industrial use is mainly obtained from wood pulp and cotton.

Paper History

Paper derives its name from the reedy plant papyrus, which the ancient Egyptians used to produce the world’s first writing material by beating and pressing together thin layers of the plant stem. However, complete defibering which is characteristic of true papermaking was absent (Smook, 2016). The first authentic papermaking, which is the formation of a cohesive sheet from the rebonding of separated fibers, has been attributed to Cai Lun who was born in Guiyang (modern day Leiyang) in China, although recent archaeological evidence points to the invention of papermaking occurring 200 years earlier in Dunhuang in China’s northwest Gansu province. In CE 105, Lun used bamboo, mulberry bark, hemp, silk and rags (his exact formula has been lost) to make paper in forms recognizable today as paper (as opposed to papyrus). Although early forms of paper had existed in China since the 2nd century BCE, Lun was responsible for the first significant improvement and standardization of papermaking by adding essential new materials into its composition (Needham and Tsien, 1985). However, the secret of paper manufacture did not begin to spread beyond the Chinese region until the 7th and 8th centuries CE. The dispersal of paper has been very precisely traced: from Samarkand in 751; Baghdad in 793; Egypt in 900; Morocco in 1100; and Italy, 1276. Paper was used in Cologne in 1320 and in Nuremberg by 1391 (Carlisle, 2004).

A persistent theme throughout history is that packaging is made from the lowest cost materials, and for a long time, paper was too expensive to be used for packaging as it was hand-made from rags for 17 centuries after its invention. However, by 1702 the cost of paper had become cheap enough that it could be printed on and then thrown away, giving rise to the world’s first daily newspaper - the Daily Courant published in London.

Many fibers have been used for the manufacture of paper including those from flax, bamboo and other grasses, various leaves, cottonseed hair and the woody fibers of trees. The influence of the raw material can be largely assigned to the length and wall thickness of the fibers rather than to their chemical composition. Paper use was hindered by the laborious process of papermaking and the limited supply of raw materials until the invention of processes for pulping straw, wood, and wastepaper in the 1850s. The ability to make paper from abundant natural resources has made it an inexpensive commodity with a wide range of packaging applications. The most significant role of wood in packaging today is the use of its fibers for the raw material for paper and paperboard (Twede et al., 2015). Today, about 97% of the world’s paper and board is made from wood pulp, and about 85% of the wood pulp used is from coniferous forests consisting mostly of pines, spruces, firs and larches of the north temperate zone.

With the increasing demand for paper, existing accessible wood resources may be inadequate to meet this growing demand. It is, therefore, necessary to consider non-wood pulp to meet the possible shortfall of wood fiber for papermaking. Bamboo and other potential non-wood materials will become more popular in the pulp and paper industry.

Pulping

Pulp is the fibrous raw material for the production of paper, paperboard, corrugated board and similar manufactured products. Pulping refers to the process wherein wood or other fibrous raw materials are reduced to a fibrous mass, the purpose being to separate the cellulosic wood fibers by breaking down the wood’s inter-cellular lignin glue, without damaging them so that they can then be reformed into a paper sheet in the papermaking process. Pulping is accomplished by either mechanical, thermal, chemical or a combination of these treatments. The most prevalent process is chemical pulping, which accounts for more than 70% of the worldwide production of pulp, of which kraft pulping is the most prevalent at 80% (Kadla and Dai, 2006).

The first process for the manufacture of chemical wood pulp was invented by Englishmen Charles Watt and Hugh Burgess in 1851. When their invention aroused little interest in England, they emigrated to the US, established a mill on the Schuylkill River near Philadelphia, and received a patent (US 11,343) for their soda process in 1854. In France in 1853, Theodore Coupier and Marie Amedee Charles Mellier patented a soda process (US patent 9910) to disintegrate cellulose pulp from straw based on a 1851 invention for “a new and improved method of reducing fibrous vegetable substances to pulp fit for the purpose of making white paper”, to quote from their patent which preceded that of Watt and Burgess. The soda process consisted of boiling wood in 4–6% sodium

hydroxide liquor at a high temperature (170 °C). A later patent in 1865 covered the incineration of the spent soda liquor to recover most of the alkali used in the process (Smook, 2016). Less than 2% of the pulp produced today uses this process which is very similar to the sulfate process except that only sodium hydroxide is used. Essentially all former soda mills have converted to the sulfate process.

In 1879, German chemist Carl F. Dahl developed the sulfate method of pulping wood by using sodium sulfate instead of sodium hydroxide as the cooking liquor. The new sulfate process produced a much stronger pulp which is more commonly known as kraft pulp after the German and Swedish word for strength. Although Dahl commenced construction of a kraft mill in his native Germany, it was never completed due to lack of finance (Ainsworth, 1959). He moved to Sweden and the first kraft mill was built in Munksjö, Sweden in 1885. The first kraft mill in the US was the Roanoke Rapids Paper Manufacturing Company (later changed to the Halifax Paper Company) in North Carolina which opened in 1909. Today, the sulfate process is the dominant chemical wood pulping process.

The invention of the sulfite process is generally credited to the American chemist Benjamin Chew Tilghman who, in 1857, found that wood could be softened and defibered with a solution of calcium bisulfite ($\text{Ca}(\text{HSO}_3)_2$) and sulfurous acid. Together with his younger brother Richard, Tilghman started the first industrial experiments to produce pulp from wood by treatment with hydrogen sulfite. This was 1866 at the paper mill Harding and Sons, Manayunk, close to Philadelphia. Swedish chemist Carl Daniel Ekman treated wood with magnesium bisulfite in 1870 and constructed the first sulfite paper mill in 1872 in Bergvik, Sweden. A German modification of the American sulfite process was developed by the German chemist Dr Alexander Mitscherlich and involved cooking (using indirect steam heating) at lower temperatures and pressures and for longer times than previously used. This was the dominant pulping process until 1937 when kraft pulping became the foremost chemical pulping process. The invention of the recovery boiler by G. H. Tomlinson in the early 1930s allowed kraft mills to recycle almost all of their pulping chemicals. This, along with the ability of the kraft process to accept a wider variety of types of wood and produce stronger fibers, made the kraft process the dominant pulping process. By 1900 approximately 5200 pulp and paper mills existed worldwide with approximately 1300 in Germany, 512 in France, and the remainder mostly in the US (Kamm et al., 2015).

Papermaking

In 1790, French soldier and mechanical engineer Louis-Nicolas Robert became an indentured clerk at Pierre-François Didot's papermaking factory in Corbeil-Essonnes, working under Saint-Léger Didot. Robert applied for a French patent for his machine in 1798 and it was granted the following year (dossier 1BA95). His machine had a moving screen belt that received a continuous flow of stock and delivered an unbroken sheet of wet paper to a pair of squeeze rolls. As the continuous strip of wet paper came off the machine it was manually hung over a series of cables or bars to dry. This continuous, unbroken sheet of paper later had to be cut into separate sheets.

Robert and Didot quarreled over the ownership of the invention and Robert eventually sold both the patent and the prototype machine to Didot for 25,000 francs. Wanting to develop and patent the machine in England away from the distractions of the French Revolution, Didot sent his English brother-in-law, John Gamble, to London. Gamble was granted British patent 2487 in 1801 for an improved version of Robert's original machine after agreeing to share the London patent application with brothers Sealy and Henry Fourdrinier, two prosperous London stationers who purchased the patent interests of Didot. Gamble and Didot shipped the machine to London, and after 6 years and approximately £60,000 of development costs, the Fourdriniers were awarded new patents. Gamble commissioned the engineering firm of Hall to build a prototype. The task was assigned to one of Hall's apprentices, Bryan Donkin (who was also involved in the development of the tinplate can) who installed the first production machine at Frogmore Mill in Hertfordshire in 1804. The first US Fourdrinier machine was built in England by Donkin, and began operation in 1827 at Saugerties, NY.

The Fourdrinier brothers spent the whole of their private fortune in developing a practical paper machine, eventually becoming bankrupt and dying in poverty, as also did Louis-Nicolas Robert. Despite their misfortune, the Fourdrinier name has been familiar to generations of papermakers for the development of a machine, the essential principles of which are still in use today (Fig. 3).

A second system was developed in 1809 by John Dickinson of England and is known as the cylinder or vat machine process. A cylinder covered with a wire cloth is rotated partially submerged in a stock suspension and a vacuum applied inside the cylinder, resulting in water draining inward through the wire cloth, and the paper web forming on the outside. Cylinder machines are used to produce heavy multi-ply boards.

The twin-wire method for forming paper and paperboard was developed in the UK at St. Anne's Board Mill, Bristol in the 1950s. A typical twin-wire forming unit is the Inverform, which was designed to provide a new method for the manufacture of single and multi-ply sheets at high speeds.

Paper-Based Packaging

Prior to the 1800s, most of the references to paper-based packaging are for unprinted wrapping or bags used by merchants. Retailers would purchase products in barrels and weigh out and use paper to wrap up a quantity for each consumer.

Before 1817 all paper in the US was made by hand. In order to produce a thick board, handmade sheets of paper were coated with an adhesive substance and then pressed together. The first paper machine operated in the US (the cylinder machine) was

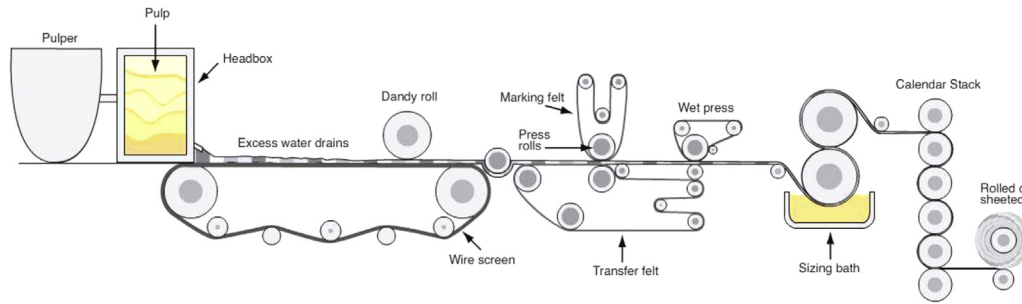


Figure 3 Fourdrinier machine for making paper. <https://www.strathmoreartist.com/faq-full-eu/how-is-paper-made-705.html>.

patented by Thomas Gilpin, of Wilmington, Delaware in 1816 and was a variation on Dickinson's design. Joshua Gilpin, brother of Thomas, had introduced to the US the technique of bleaching paper with chlorine in 1804. Charles Kinsey of Paterson, New Jersey had already patented a continuous process papermaking machine in 1807 and was successfully making paper at the Essex Mill in Paterson by 1809. Financial stress persuaded Kinsey and his backers to change the mill's focus from paper to cotton and Kinsey's early papermaking successes were soon overlooked and forgotten.

Gilpin's machine, with many added improvements, forms the backbone of the paper-board industry of today. Presses, driers, and calenders were added to Gilpin's machine shortly after its introduction, and by the mid-1800s, most paper mills were equipped with fourdrinier or cylinder paper machines.

The 1860s and 1870s were known as the 'Age of Paper' as this was when the acceleration in the use of paper for packaging started. As the 1800s drew to a close, the developments in printing and papermaking gave birth to the package converting and filling industries. Paper-based packaging was ready to move onto the center stage of grocery shelves.

At the same time, the grocery shelves (especially in the US) were being transformed by the development of chain stores, and the relationship with the consumer was passing from shopkeepers to brand manufacturers. Mass production required mass-produced packages, and mass marketing required a print media to carry the sales message. As well, mass distribution required an inexpensive disposable shipping container, and the new supply of paper was well positioned to meet the new demand (Twede, 2012).

Folding cartons are containers made from a sheet of paperboard that is scored, folded, glued to form a tube and folded flat for shipment to the filler, where they are erected, filled and closed with tuck flaps or glue. Although the early folding cartons were relatively expensive and produced in small numbers, the demand outstripped the supply (Twede, 2012). A prototype of a folding box was patented in 1879 by Italian inventor Charles E. Bolchini of Milan, Italy (US patent 218,479). Bolchini's box was cut from a single piece of paper and formed a three-sided prism-shaped container.

Although attributed to a factory mistake, the more optional folding carton came on the scene in 1879, courtesy of the Robert Gair Company of Brooklyn, New York. Founded by Robert Gair, a Scottish-born immigrant, he was a printer and paper bag maker in Brooklyn, New York in the 1870s. In 1891, Matthew Vierengel, a "practical machinist, inventor and draughtsman" in New York assigned his patent (US 463,849) for a machine for making plaited boxes or similar articles to the Robert Gair Company. Vierengel's intention was, "first, to form a blank into a box, cup, cap, or similar article and fold or gather the sides of the same into plaits by one operation; secondly, to transfer the article after being formed and platted to edging, pressing, and embossing dies, so that the successive operations shall be performed on the article automatically".

Gair held several design patents for boxes. In 1894 his paper box patent (US 519,451) comprised "a new construction of such boxes, consisting in altering the position and shape of the slots in order that the end flaps may make a more secure connection with the turned-in parts, and also in arranging the turned-in parts to interlock and thereby, when the box is set up, the sides shall be held together positively by the turned-in pieces for additional strength and security".

Gair's most famous carton was for Uneda Biscuit, the first branded cracker sold in a moisture-barrier package, through a national marketing campaign. It has been hailed as the "first consumer package," symbolizing the end of the unsanitary cracker-barrel era and the birth of 20th century mass-marketed shelf-stable food, with an advertising strategy that tells the consumer what "you need". This overstates its significance, since there were clearly other consumer packages at the time and earlier, but none were so spectacularly successful (Twede, 2012) (Fig. 4).

Gair died in 1927, and his obituary credited him with a "revolution in the retailing of goods". At that time, his company was the largest in the industry, producing 18% of the paperboard and containers in the US (Twede, 2012).

Another significant invention in the early 1800s set the stage for modern packaging: color printing of illustrations. Lithographic printing was to become particularly well suited to mass reproduction of multi-colored designs on packages at a relatively low cost. Combined with the papermaking machine and the wood pulping processes, it brought the cost of illustrated paper-based packaging low enough so that its marketing value outweighed its cost (Twede et al., 2015).

Many specialty papers for wrapping were developed. By the 1900s, properties were tailored to the product intended to be wrapped, and most had names that reflected their use. Greaseproof and glassine paper for baked goods, bleached water-resistant butcher paper for meat, pouch and envelope papers, and other specialties like cartridge paper and tissue paper were common. Many of these paper-based packages have since been replaced by plastic films and laminations.



Figure 4 Uneeda biscuit advertisement featuring a boy in a raincoat to emphasize the moisture barrier properties of the carton. From <http://www.randysusanmeyers.com/blog/2018/11/the-year-google-and-goya-saved-thanksgiving/>.

Molded Pulp

The term “molded pulp” is used to describe a three-dimensional package that is used for protective packaging, food service trays and beverage carriers. The highest volume molded pulp packaging has been for eggs, a purpose for which it is still used. It is manufactured from an aqueous slurry of cellulosic fibers and formed into discrete products on screened molds (Waldman, 2009).

In the mid-1800s, with the mass distribution of newspapers and books, the prices for paper-related products dropped, and thus, with the increased availability of pulp, new applications emerged. The first appearance of a method for making molded products from wood pulp dates back to 1890. The first patent for a machine for molding articles from pulp (US 759,616) was granted in 1904 to Martin L. Keyes from Cambridge, Massachusetts (Didone et al., 2017). The process differed from papermaking in that the mold was three-dimensional. Molded pulp can be made completely from scrap or recycled material, typically paperboard and newsprint, and can later be recycled with other paper products. With its high strength, durability and low cost, molded pulp can be a replacement for wood and plastics. An innovative way of drying the products based on the concept of impulse drying can be exploited for the production of precision molding products, because the drying is performed in a more controlled way than the free dried operations.

Since the late 1980s, consumers have developed an interest in the environmental impacts of the packaging which contains the products they buy, and the molded pulp industry has responded by developing new and innovative packaging.

In recent years, there has been considerable publicity about the development of paper bottles. The GreenBottle[®] was invented in 2005 by Martin Myerscough in the UK and consisted of a molded pulp outer with an inner plastic pouch complete with screw cap. Despite being trialed for milk and wine, it has not enjoyed commercial success. Founded in 2008, Ecologic Brands based in Manteca, California developed eco.bottle[®], consisting of a molded pulp outer shell and an inner plastic pouch made from LDPE with a patented resealable spout made from PP. Both packages are basically bag-in-box technology: a paperboard shell for rigidity with an LDPE internal pouch to hold the product. Ecologic has been manufacturing its eco.bottles in California since 2013 and is now looking for the right strategic partner to help scale-up production.

In 2008, Jim F. Warner invented the concept for a 360 Paper Water Bottle[™] and filed the initial patent the following year; US 8,701,905 was granted in 2014 and assigned to Double Double D, LLC, Waynesville, Ohio. Paper Water Bottle[®] is based near Cincinnati, Kentucky and in 2016 successfully prototyped an eco-friendly replacement for plastic water/beverage bottles with a shell made entirely of renewable molded fiber, with an internal barrier of 100% recycled resin that requires less plastic than a standard plastic bottle. Based on 16 global patents, production of the Paper Water Bottle Eco-1 commenced in December 2017. Today, the products are made of 65% compostable material but the ultimate aim with the third generation Eco-100 is to reach Backyard Compostable[™] disposability (Fig. 5).

In 2015 Danish brewer Carlsberg announced their ambition to develop the world’s first fully biodegradable wood-fiber molded pulp bottle in conjunction with ecoXpac (which owns the rights to an energy-saving impulse-drying technique) and the Technical University of Denmark. All parts of the Green Fiber Bottle — including the cap — are to be manufactured using only biobased and biodegradable materials. The first prototype based on the distinctive Carlsberg design was revealed in 2015 but there has been little news since. The Green Fiber Bottle project aims to make a fully molded paper bottle, removing the need for an inner liner and making the bottle completely biodegradable. A consortium of industrial and academic partners is collaborating with Carlsberg A/S, which aims to package its beer in the new bottle.

Beverage Cartons

According to Elopak (2007), Gustav Türk from Kronstad, Sweden patented a paper-based beverage container as early as 1882. It was impregnated with a combination of fine limestone powder, aluminum-oxide and fresh blood serum. No record exists of its commercial success or indeed the patent.



Figure 5 Green Fiber Bottle prototype and Paper Water Bottle[®].

Dr. Hervey D. Thatcher, a Potsdam, New York, druggist, who also developed some of the earliest glass milk bottles, applied for a patent for a waxed paper milk pail in 1895 and was granted US patent 553,794 in 1896. Thatcher discussed many of the issues connected with glass milk bottles (including breakage as well as problems with sanitation and washing) and claimed that his "Paraffined Pail" would solve the problems with glass. He followed up with two other patents in 1899 and 1901 for refinements but never advanced beyond the "pail" design.

The first records of paper being used to carry liquids on a commercial scale are found in reports, dated 1907, from a Dr Winslow of Seattle. He noted that "the latest departure in the way of a milk bottle is the single service milk container of wood-paper made and invented by G.W. Maxwell of San Francisco ... now in actual use by dairymen in Los Angeles." George W. Maxwell and Alonzo Kingsbury applied for the patent in 1905 and received US patent 827,984 for a 'Milk Receptacle' in 1906, although Kingsbury assigned his portion to Maxwell. Paraffin wax was used to moisture-proof the paper but achieving a liquid-tight bond at the joins was more difficult. The paper cover was wedged into place and held by four tabs (Fig. 6).

In 1915, John Van Wormer, owner of a toy factory in Toledo, Ohio was granted US patent 1,157,462 for a 'paper bottle' (actually a folded blank box) for milk that he called Pure-Pak. The crucial and unique feature was that this box would be delivered flat to be folded, glued, filled and sealed at the dairy. The milk was accessed by pushing open the gables at the top back and pulling the top (spout) out. This package offered significant savings in delivery and storage in comparison with preformed glass bottles, then the predominant package for milk, having been introduced in 1889. The challenge came with the design of the machinery to be sold or leased to the dairy to form, fill and seal the cartons (Robertson, 2002) (Fig. 7).

In 1928, the American Paper Bottle Co. acquired the Van Wormer patents and the Pure-Pak trademark and apparently hired him at the same time. It built the first six machines from 1929 to 1934, while striving to perfect both the container and machinery. In the early 1930s, it promoted its Pure-Pak milk containers to dairies and consumers, but it faced competition from other paper-based packages. By the 1930s, some ten companies had introduced some kind of paper package for milk in the US. For example, Sealcone (cone-shaped) containers were introduced in New York in 1929 and included American Can Co.'s Canco package and Sealright's Megaphone, but most were short-lived.

In 1934, American Paper Bottle Co. approached Ex-Cell-O Corporation, a Detroit-based company set up by ex-Ford employees in 1919 that specialized in supplying machinery to the automobile and aviation industries, to manufacture machines to form, fill, and seal Pure-Pak cartons. Six prototypes were commissioned, but funds ran out, and Ex-Cell-O took over the rights to the Pure-Pak system as part of the settlement. Ex-Cell-O promptly began to redesign both the machinery and the package. The first Ex-Cell-O Pure-Pak filling machines were installed in 1936 at Borden's Dairies, New York, producing 24-quart cartons/min, and then later at Risdon Bros, Detroit, in early 1937. The construction principle was the same as Van Wormer's original, with the carton formed from a blank, glued at the bottom, dipped in paraffin wax, and the top folded and stapled shut after filling. These early versions had to be opened with a knife or scissors. Ex-Cell-O quickly redesigned the top with a tab on the side of the gable that could be lifted for pouring. In 1955 the "Pitcher Pour", featuring a built-in pouring spout that replaced the perforated tabs and openings covered by paper patches, were introduced. By the early 1970s, more than half of the fluid milk in the US was packaged in half-gallon Pure-Pak cartons, with another 20% in gallon cartons (Fig. 8).

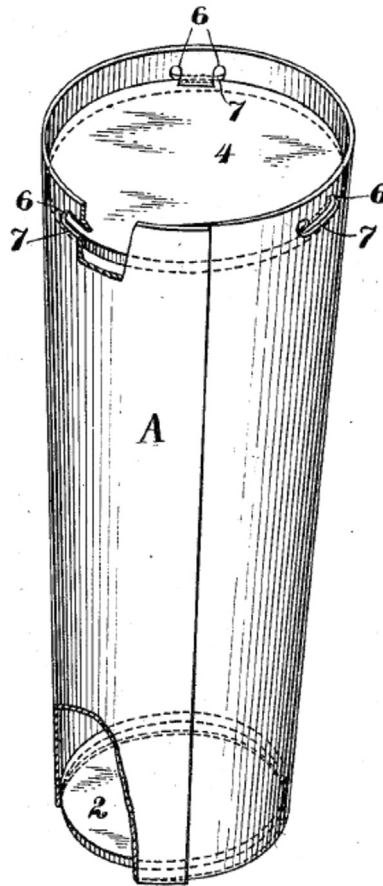


Figure 6 Drawing of milk receptacle from US patent 827,984 filed by Maxwell and Kingsbury in 1905.

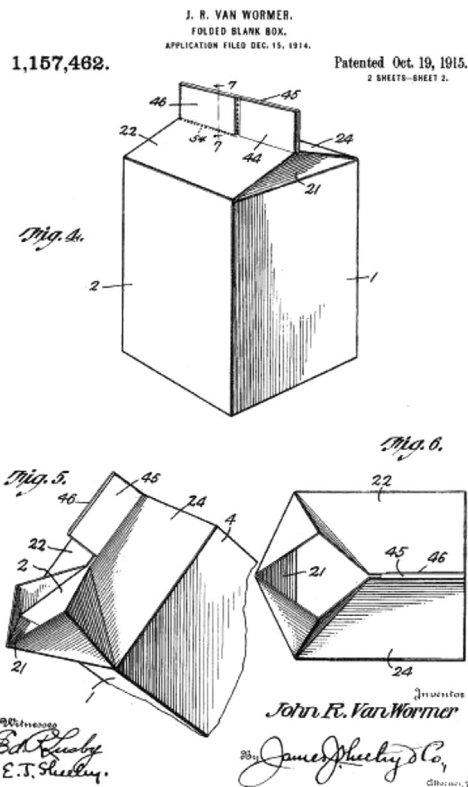


Figure 7 First patent for a gable top carton (US 1,157,462) was filed by John Van Wormer in 1915.

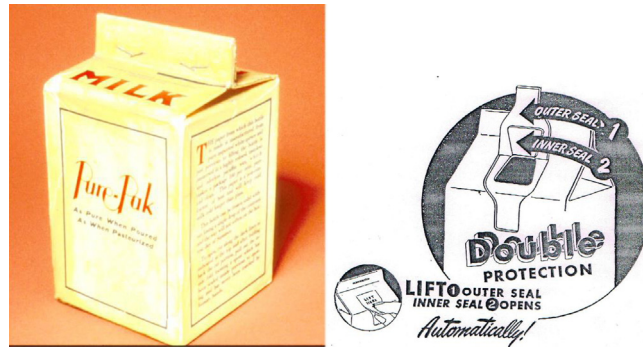


Figure 8 Pure-Pak carton showing stapled gable-top (LHS) and built-in pouring spout (RHS).

After World War II, Pure-Pak cartons arrived in Europe to supply the US troops stationed in Germany. Their demand for milk meant that the milk was imported from Austria, Denmark, France, Italy, and the Netherlands, in cartons supplied from the US. By 1957, Pure-Pak had 60% of the US milk market. The Norwegian tobacco company Tiedemanns, looking to diversify, obtained a license from Pure-Pak, partly to help supply cartons for the US troops in Germany and partly in the belief that the European market was now ready and could afford such a package. The company became known as Elopak (from European Licensee of Pure-Pak) and in 1958 the first milk in Pure-Pak cartons went on sale by Asker Dairy outside Oslo, Norway; it was promptly a big success, despite a premium price compared to bottled milk. In 1987, Elopak acquired Ex-Cell-O's Packaging Systems Division and became the owner of the Pure-Pak license worldwide. Meanwhile, in 1966 Tetra Pak began offering its own gable-top machines and cartons known as Tetra Rex on the basis of a license agreement with interested parties in the US.

The modern gable-top carton retains the simple basic geometry of earlier years although flat-topped and plastic-topped versions are available, as well as added refinements such as plastic screw caps and recloseable spouts. Incorporation of an aluminum foil layer permits longer shelf life of chilled premium juice products; in some cases, the foil is replaced by a barrier polymer such as EVOH or SiO_x-coated PET. If the foil is replaced, then the carton must be sealed using ultrasonic sealing or heated jaws rather than induction sealing.

The story of the European beverage carton began in the renowned machine works of Ferdinand Emil Jagenberg in Düsseldorf, Germany with the manufacturing of machines for the production of folding boxes. The impetus for the beverage carton followed in the 1920s when Günter Meyer-Jagenberg, a nephew of Emil Jagenberg, travelled to the US and discovered the milk cartons which were then largely unknown in Europe. Back in Düsseldorf, Meyer-Jagenberg drew on the know-how of the family-owned company that had developed a leak-proof paper "can" for marmalade consisting of a seamed carton base and a similar lid during World War I. In 1930 the company applied for a patent for 'perga', a water-resistant paper receptacle with folding closure, as well as the equipment for its production. German patent 595,935 was issued in 1934. The Perga carton was made of ribbed and paraffin-coated paper sleeves and had a circular base with a square top. In contrast to the US development, however, this carton was oriented not toward high-speed machines but rather toward the many hundreds of dairies and filling plants that wanted to fill their products into cartons without considerable investment (Fig. 9).

Production of the Perga milk carton with a capacity of 200 mL began in 1932. By 1939, 26 Perga production companies had been set up in eight countries, including Germany, England, the US, Sweden, Canada, and Australia. Although the economic and political crisis of the following years initially supported ongoing development and distribution of the new carton, funds needed for further expansion were not forthcoming.



Figure 9 Perga milk carton (left) and drawing from German patent 595,935.

Other European packaging innovations began around this time. Erling Stockhausen in Norway developed a paper milk carton together with filling equipment that went into trial production in a dairy in southern Norway during 1939 and 1940. The arrival of World War II stopped further work. In the early 1950s, the Perga pack enjoyed a renaissance, and by the 1960s, it was one of the most widely used cartons on the European market. In line with its growing share of the market, Jagenberg Werke founded its subsidiary Papier und Klebstoffwerke Linnich (PKL) GmbH in 1958.

In 1962, PKL launched a brick-shaped Blocpak system of packages and filling machines and replaced paraffin wax with polyethylene extrusion coating. Its dimensions were based on binding European pallet dimensions and, like the gable-top carton, it was a blank-fed system available in capacities up to 2 L. It gained wide acceptance and leadership, particularly in Germany, Austria, and the UK during the 1960s and 1970s and provided stiff competition to the gable-top carton. Today it is no more, having been replaced in 1979 by the Quadrobloc gable-top package. In 1975 PKL launched the Combibloc package based on pre-manufactured blanks that could produce brick-shaped aseptic and non-aseptic packages for liquid food. In 1989, PKL was acquired by the Swiss company SIG (Schweizerische Industrie Gesellschaft) laying the foundation for the present SIG Combibloc Group AG that focuses on aseptic packaging. Since 2015, it has been part of the Canadian-based private equity company Onex Corporation.

In the 1920s, the Swede Ruben Rausing, while completing a Master's degree in economics at Columbia University, New York on a scholarship from the Stockholm School of Economics, was impressed with the fresh approaches then being developed in distribution and retailing, especially self-service stores, and realized that this trend would likely follow in Europe and increase the demand for prepackaged goods. By the early 1930s, he was the sole owner of Åkerlund & Rausing, a pioneering Swedish packaging company that enabled the prepackaging of consumer units of flour, sugar, and salt, which until then had been packed at the retail outlet immediately prior to purchase. In 1943, development work commenced on a milk package to "give maximum hygiene with minimum material." The company evaluated the gable-top cartons then being introduced in the US for milk but judged that the cartons and the associated packaging machinery were too expensive to be commercially viable in Sweden.

Because of a shortage of glass and tinfoil during World War II, Åkerlund & Rausing developed Satello, a wax-coated, cylindrical paper container for jam and similar products. This was the starting point for the development of a milk package continuously formed from a reel of packaging material, and the resultant Swedish patent 131,599 was applied for in March 1944 and granted in February 1951. This package was achieved by the simple technique of sealing and cutting a tube of moisture-proofed paperboard at alternate right angles, leading to the tetrahedron-shaped carton which gave the company its name: Tetra Pak. The idea came from a laboratory assistant named Erik Wallenberg (Engwall, 2018). In 1991 Wallenberg was awarded the Grand Gold Medal by The Royal Swedish Academy of Engineering Sciences for "his ideas and efforts in the development of the Tetra Pak packaging system" (Fig. 10).

It is interesting to reflect on the context in which Rausing undertook his developments. A paper carton for milk was certainly not a novel idea. In fact, it could almost be said to be a mature technology by 1944 with the Pure-Pak carton well established in the US and the Perga pack making increasing inroads in Europe. In addition, there had been numerous other attempts in the 1920s and 30s at making a paper milk carton, but they were no longer on the market. To succeed, Rausing needed to come up with something really innovative, and he did with the idea of a continuously-fed roll of paper passing through the filling machine in contrast to all the other systems which were blank-fed.

Then began the long development process to find a way of automatically shaping, filling, and sealing the package, together with a search for suitable packaging material. A dispersion coating of polyvinyl chloride was tried and rejected. A polystyrene mixture known as S-50 was then tried and proved satisfactory and was used successfully on the first packages. In 1952, the first commercial machine from Tetra Pak to make tetrahedral cartons was delivered to a dairy in Lund, Sweden (Leander, 1996). At that time, commercial production of low-density polyethylene film from ICI was increasing, and DuPont in the US had acquired a manufacturing license. DuPont developed an extrusion coater in 1954, and Tetra Pak began coating paperboard with polyethylene instead of S-50 in 1956. Nils Andersson from Tetra Pak in Lund, Sweden received US patent 2,894,853 in 1959 for a 'Method and apparatus for extrusion coating and product'. In 1963, Tetra Pak introduced the rectangular-shaped Tetra Brik to facilitate distribution. The idea of brick-shaped cartons was adopted from the German Zu-pack, but further developed to fit the Tetra Pak roll-fed concept.

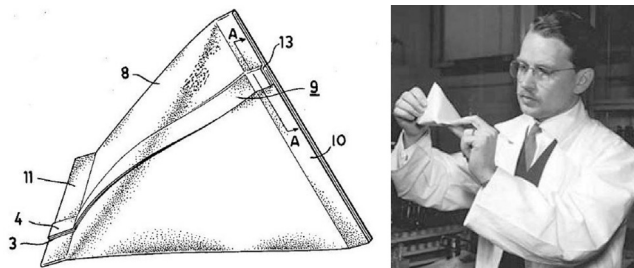


Figure 10 The tetrahedron-shaped carton described in Swedish patent 131,599 and its inventor Erik Wallenberg from Åkerlund & Rausing who later worked for Tetra Pak.

In 1968 Ex-Cell-O introduced the long shelf life packaging of fluid milk products by means of a controlled environment on their filling machines. It had long been recognized that a reduction in post-pasteurization contamination could increase the shelf life of milk (Henyon, 1999). Thus began a new concept in the US dairy industry that today is known as ESL or extended shelf life. Originally targeted at slow turnover products such as whipping creams and coffee creamers, it is now increasingly being utilized globally for the full range of liquid dairy products.

Regenerated Cellulose Film

Regenerated Cellulose Film (RCF), more commonly referred to as cellophane, is applied to films based on cellulose hydrate (regenerated cellulose). While cellophane remains a trademark in many countries in Europe and elsewhere, in the US it is, by a court decision, a generic name. Outside of the US the term transparent cellulose film (TCF) is often used rather than RCF; the latter term will be used in this article. Cellophane emerged from a series of efforts conducted during the late 19th century to produce artificial materials by the chemical alteration of cellulose (Woodings, 2001).

Swiss chemist George Audemars first manufactured regenerated nitrocellulose fibers in 1855 but they had the drawback of being highly flammable. French scientist and industrialist Count Hilaire de Chardonnet perfected the production of nitrocellulose fibers, but their manufacture was relatively uneconomical. In 1891 the British chemists Charles Frederick Cross, Edward John Bevan, and Clayton Beadle discovered that cotton or wood cellulose treated with sodium hydroxide and carbon disulfide dissolved as cellulose xanthate following the conversion of the hydroxyl groups to xanthate. They patented the process (British patent 8700) and as the solution was quite viscous, they gave this material the name "viscose." In 1893 they formed the Viscose Syndicate to grant licenses, and in 1896 formed the British Viscoid Co. Ltd. to exploit the process. In 1904 the British rights of the viscose process were purchased by Courtaulds Ltd. who produced the first commercial viscose rayon or artificial silk in England in 1905; in 1910 it was produced in the US by the American Viscose Company. Although the term 'rayon' was officially accepted in the US in 1924, in Europe the term 'viscose' remained in use for the solution used to make both cellophane and rayon.

In 1898 Charles H. Stearn was granted British patent 1020 for producing films from the substance, but it was not until 1908 that Jacques Edwin Brandenberger, a Swiss chemist, designed a machine for continuous production of a strong, transparent film. In 1905 Brandenberger had tried spraying a tablecloth with a viscose solution so that it would repel liquids such as wine rather than absorb them. Although the coated tablecloth was far too stiff for practical use, he found that the coating could be peeled off like skin. Three years later, he designed a machine to produce a material he called 'cellophane' from the first syllable of 'cellulose' and the last syllable of the French word 'diaphane' meaning translucent.

By 1912, Brandenberger was making a saleable thin flexible film used in packaging and over the eyepieces of gas masks. He obtained patents on the machinery and the essential ideas of his process and his chief improvement over earlier work was to add glycerol to soften the material. In 1917, the largest French manufacturer of rayon, Comptoir de Textiles Artificiels, agreed to finance Brandenberger's work and formed a special company, La Cellophane SA, for its production; Brandenberger assigned his patents to this entity and joined the company. After several years of further research and refinements, production and marketing of cellophane for industrial purposes began in 1920. In 1923, the American firm of DuPont, which had worked with Comptoir de Textiles Artificiels in production of rayon, set up a separate firm, DuPont Cellophane Company. The French firm transferred the patents, manufacturing processes, and know-how to the American company, which began producing cellophane in 1924 (Carlisle, 2004).

Whitman's candy company initiated use of cellophane for wrapping its high-end line of chocolates (Whitman's Sampler) in the US in 1912 and remained the largest user of imported cellophane from France until 1924. However, because cellophane was permeable to water vapor, it was unsuitable for packaging moisture-sensitive foods until DuPont chemists William Hale Charch and Karl Edwin Prindle developed a nitrocellulose (partially nitrated cellulose) lacquer in 1927 (Hyden, 1929). Interestingly, while working for the Dobeckmum Company based in Cleveland, Ohio in 1932, Prindle also invented tear-tape used to open billions of cellophane-wrapped cigarette and chewing gum packages. Heat-sealing coatings were introduced in 1931, leading to the market for high-speed overwrapping of consumer goods, and polyvinylidene chloride copolymer coatings were commercial in 1949, thereby further increasing the potential applications for better barrier properties and thinner films (Sineath and Pavelchek, 1971).

When cellophane was first made by DuPont, wax paper, glassine, and sulfite paper were the major flexible packaging materials in use. Cellophane was the earliest transparent packaging material used for foods. According to a 1949 study in the US, of the total amount of transparent packages, cellophane accounted for about 87%. DuPont's cellophane, including both moisture-proof and other types, amounted to 78% of all the cellophane produced and imported. Food packaging accounted for about 80% of DuPont's cellophane sales in 1949 (overwrapping of cigarette packages was about 11% of DuPont's total sales of cellophane).

A joint venture company British Cellophane Ltd (BCL) was formed in 1935 between La Cellophane SA and Courtaulds, and a major factory for producing cellophane was built in Bridgwater, England. Since 2004 it was owned by Innovia Films Ltd, UK and is now owned by Futamura Chemical Co. Ltd with production sites in Japan, UK and the US Sales of cellophane have declined in recent years from a peak in 1960 as a result of alternative packaging options, in particular oriented polypropylene.

It is important to note that RCF is not a thermoplastic as it will not melt and cannot be formed by pressure and heat. Regenerated cellulose is manufactured from highly purified cellulose usually derived from bleached sulfite wood pulp or, to a limited extent, cotton linters, and can be regarded as transparent paper. As well as packaging a variety of foods, there are other industrial applications such as a base for self-adhesive tapes.

A change in the growth of the cellophane industry in the US from positive to negative began around 1960 and was initially due to low density polyethylene films, which by 1962 grew to a total tonnage comparable with RCF. Competition from PVC films also

played a part in one market segment (packaging of fresh meat). By and large, direct competition between RCF and polyethylene films was rather limited, except in the area of bread wrapping, because polyethylene, although substantially cheaper than RCF per unit area, was not suitable for use on most wrapping machines developed for RCF. However, polyethylene entered other new markets (e.g. fresh produce packaging) which would have used RCF if polyethylene had not been available and was mainly responsible for RCF growth halting around 1960 (Cowley, 1985).

A working paper by Hisano (2017) examined how innovations in transparent packaging, specifically cellophane, in the mid-20th century helped US retailers create full self-service merchandising systems, including those that sold perishable food. While self-service stores began appearing in the late 1910s, self-service was initially applied only to grocery and dry goods, such as canned foods and a box of breakfast cereals. It was not until after World War II that the majority of American grocers adopted self-service to meat and produce sections. However, the significance of the development of cellophane as a new packaging material, and the role of packaging manufacturers in promoting self-service, has yet to be analyzed. Hisano (Hisano, 2017) showed how the expansion of self-service operation and the increasing use of transparent packaging had a significant impact not only on how consumers purchased foods but also on how they understood food quality (Fig. 11).

Cellulose Acetate

In 1865, French chemist M. Paul Schützenberger produced the first organic ester of cellulose (cellulose triacetate) by heating cotton and acetic anhydride to about 180 °C in a sealed tube until the cotton dissolved. Uniquely, it had a degree of substitution (DS) of about three but was soluble only in expensive solvents. In 1894, two British chemists, Charles Frederick Cross and Edward John

SELF SERVICE

**New SELF-SERVICE MEATS
Make Shopping Quicker, Easier**

You help yourself to the cuts you want
—packaged in Du Pont Cellophane—

Here's the pleasing new way to buy meats—*self-service*, just like other foods. Pre-cut, weighed, priced and wrapped in Cellophane right in the store . . . displayed in open, refrigerated cases. You select the cut you want, all trimmed and ready . . . you waste no time. Cellophane lets you see exactly what you buy . . . keeps the meat fresh and clean.

More and more leading food stores now sell meats this new way. When it comes to your community, we're sure you'll like it, because it's so convenient and time-saving.

A few of the many meats sold this way:

ROAST POULTRY BAM

HAMBURGER FRANKS EDMITS COLD CUTS

DU PONT
Cellophane

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

Figure 11 Advertisement for DuPont Cellophane, Saturday Evening Post, 1949. dpads_1803_00320, Series 1, Box 43, Folder 27, DuPont Advertising Department records (Accession 1803), Manuscripts and Archives Department, Hagley Museum and Library, Wilmington, DE.

Bevan, took out a patent for the manufacture of filaments and films from chloroform solutions of this triacetate. Although it was not an economical process, it became the industrial process for the manufacture of cellulose acetate following further work by the Swiss brothers Camille and Henri Dreyfus. In 1905, they developed the first commercial process for the manufacture of CA, producing lacquer and film at Basel in 1910.

Cellulose acetate (CA) was originally used for photographic film as a replacement for the unstable and highly flammable nitro-cellulose film. Although CA (like cellophane) is made from cellulose, it has very different properties. Unlike cellophane, it is thermoplastic, that is, it will soften and melt when heated and therefore is easier to process. CA can be broadly classified into cellulose diacetate (CDA) and cellulose triacetate (CTA) with a degree of acetylation (degree of substitution of hydroxyl groups) of about 2.4 and 2.9 respectively. The two types of CA have different physical and mechanical properties. In general, with increasing acetyl content, the permeability to gas and moisture decreases whereas the chemical resistance, glass transition temperature and modulus increases.

CA has a high rate of water vapor and gas transmission, and this property was used to advantage in the packaging of fresh fruits and vegetables. Because it has a low static attraction for dusts, it was also used as a window in foods that generate dust such as pastas. It can also be used as a semirigid container or as a thermoformed blister package, but today it finds very limited use in food packaging.

CA was first used for food packaging in 1931 and, like RCF, was also highly transparent but not moisture-proof. By 1949, sales of CA were only 3.7% of RCF sales in the US. Celanese is the world's largest commercial manufacturer of cellulose diacetate films with a range of acetate films in a variety of gauges from 14 μm to 500 μm .

Metal Packaging

Four metals are commonly used for the packaging of foods: steel, tin, chromium and aluminum. Tin and steel, and chromium and steel, are used as composite materials in the form of tinplate and electrolytically chromium-coated steel (ECCS), the latter being somewhat unhelpfully referred to as tin-free steel (TFS). Aluminum is used in the form of purified alloys containing small and carefully controlled amounts of magnesium and manganese.

Metal cans are commonly called tin cans although many have no tin and even tin cans are mainly steel. The word 'can' is an American abbreviation of the English "canister", a word for box derived from the Greek "kanastron" which was a reed basket.

Today, materials like tinplate and aluminum have become universally adopted for the manufacture of containers and closures for foods and beverages, largely due to several important qualities of these metals. These include their mechanical strength and resistance to working, low toxicity, superior barrier properties to gases, moisture and light, ability to withstand wide extremes of temperature and ideal surfaces for decoration and lacquering (enameling).

History of Canned Foods

Modern tinsplating technology began in Bohemia in the early Middle Ages and the first commercial manufacture of tinplate commenced in England in 1699 and in France in 1720, where it was used for a variety of purposes including for household utensils such as plates. Sometime in about the middle of the 18th century, the Dutch navy began to use preserve foods by packing them in fat in tinned iron canisters (Thorne, 1986). After cooking and while still hot, the material to be preserved was placed into the canister, covered with hot fat and the lid immediately soldered on. Records show that from 1772 to 1777, the Dutch Government supplied its navy (which had been sent out to Suriname [formerly Dutch Guiana in South America] to quell a revolt) with roast beef packed in this way (Farrer, 1980).

Before the end of the 18th century, the Dutch had also established a small industry to preserve salmon in a similar manner. Freshly caught salmon were cleaned, boiled in brine, smoked over a wood fire for 2 days and then placed in a tinsplated iron box. The gaps between the fish were filled up with hot salted butter or olive oil and a lid was soldered onto the box (Thorne, 1986). A famous London firm of snuff merchants supplied 13 tins of Dutch salmon to one of its clients in 1797 (Farrer, 1980). Thus, a canning industry of sorts had been established in Holland independently of, and prior to, Appert's work.

Lazzaro Spallanzani was born in Scandiano, Italy in 1729. He entered a Jesuit college at the age of 15 and later studied law at Bologna but became interested in physics and developed an overall knowledge of the natural sciences. He took holy orders in 1755 and is therefore often referred to as the Abbé Spallanzani. In 1768 he published his theory of the spontaneous generation of microbes. In a series of experiments, he showed that meat extracts, when boiled, did not produce these forms if placed in vials that were immediately sealed by fusing the glass. Spallanzani's influence on future developments was more than passing, culminating in the epic work of Louis Pasteur (1822–95) nearly a century later (Doetsch, 1976).

The Frenchman Nicolas Appert (1749–1841) was a confectioner and chef in Paris from 1784 to 1795. In 1790 he set up his first bottling plant at Massy, near Paliseau, just outside Paris (Graham, 1981) where he began experimenting with ways to preserve foods, succeeding with soups, vegetables, juices, dairy products, jellies, jams, and syrups. Initially Appert used glass bottles with large openings, and glass jars. These big containers were specially made for his purposes and were closed with cork stoppers that were secured by two crossed wires. The sealed containers were placed in a boiling water-bath for a time that depended on the type of food. Appert may have known about Spallanzani's discovery, for his process of canning was based on the same principle. Records indicate that sailors tasted Appert's products in 1803.

There are two myths that have grown up in relation to Appert and his development of what became the canning process. The first is the quote attributed to Napoleon that “An army marches on its stomach.” This quote has also been attributed to Frederick the Great and Claudius Galen (CE 130–210), chief physician to the Roman army. While its origin is debatable, its truth is self-evident. The second myth is that in 1800 Napoleon offered an award of 12,000 francs to anyone who could devise a practical method for food preservation for armies on the march. Although Napoleon was Emperor of France from 1804–14 and briefly in 1815, it is unlikely that as an army General in 1800 he was in a position to offer a reward. A valuable paper by two staff from the National Conservatory of Arts and Crafts in Paris (Garcia and Adrian, 2009) has told the true story behind the 12,000 franc payment that Appert received (Fig. 12).

Appert asked for assistance from the Ministry of the Interior’s Bureau of Arts and Manufactures in 1809. The minister offered him two options: he could patent the process and receive the royalties; or he could publish complete details of his preserving process. If he chose the latter, he would receive a considerable grant of 12,000 francs from the French government (as a rough comparison, in 1840 a professor working in Paris had an annual salary of 5000 francs). Appert chose the second proposal and in 1810 published all the useful data and tips. The book entitled “The art of preserving all kinds of animal and vegetable substances for several years” had a print run of 6000 copies and 200 were sent to the Ministry of the Interior who gave one copy to each French subdivision. A second edition with a print run of 4000 copies appeared in 1811; a third in 1813; and a fourth in 1831. A German translation was published in 1810 and an English one in 1812. After the destruction of the manufacturing facility by foreign troops in 1814, and again in 1815, Appert received a silver medal from SEIN (an institute devoted to the development of industrialization in France) in 1816 and a gold medal in 1820. He expected further financial help but had to wait until 1824 when he received a prize of 2000 francs from SEIN (Garcia and Adrian, 2009). In 1827 SEIN awarded him a gold medal, and in 1836 he was granted a life annuity by the Government of 1200 francs per year.

Appert used glass containers until he travelled to London in 1814 where he discovered that metallurgy was more developed than in France and as a consequence food was put into soldered iron cans; he also discovered that steam rather than boiling water was used for sterilizing the food (Garcia and Adrian, 2009). Appert deliberately avoided tins in his early work because of the poor quality of the French product, according to the fourth (1831) and fifth (1858) editions of his book.

Unfortunately, Appert never profited from his innovation; he died alone and destitute in 1841 at the age of 91. However, the importance of Appert’s discovery in the field of food technology justifies his posthumous fame. Bitting (1937) coined the name “Appertizing” in honor of Appert but it never became widely accepted and the term “canning” remains in common usage (Fig. 13).

After almost two centuries of history, there is still controversy as to who introduced the “tin” can as a package (Cowell, 1995). The latest account, based on extensive research of early-nineteenth-century archives (Cowell, 2007), has thrown additional light on those involved in the genesis of the canning industry and revealed a new name: the French inventor Phillipe de Girard who was likely a French émigré who settled in England during the French revolution. It appears that he got English merchant Peter Durand (1766–1822) to patent the process in 1810. The patent (GB 3372) granted on August 25, 1810 by King George III of England, was for a method of preserving animal food, vegetable food and other perishable articles using various vessels made of glass, pottery, tin or other suitable metals with a focus on the preservation technique rather than the container. A successful trial with the Royal Navy was undertaken at Durand’s request in 1811, and the patent was acquired by Bryan Donkin in 1812 for which Girard received £1000. Donkin had become interested in the tinning of iron as early as 1808 and, as mentioned earlier, was involved with John Gamble in developing the Fourdrinier papermaking machine.

Donkin applied to the British Admiralty for a test of his product and the first substantial orders were placed in 1814 with the London firm of Donkin, Hall and Gamble for meat preserved in tins (John Hall was the founder of the famous Dartford Iron Works). By the 1820s, canned foods were a recognized article of commerce in Britain and France. Donkin’s early cans

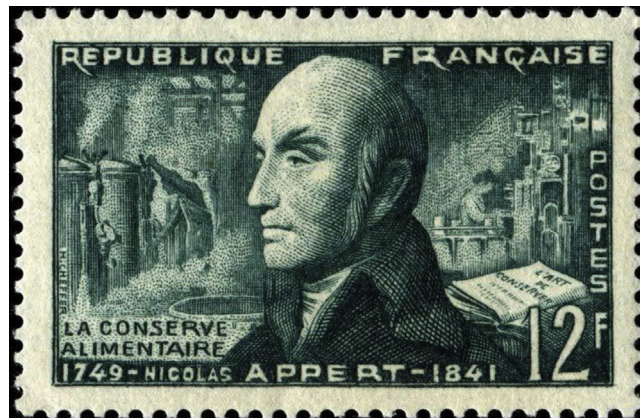


Figure 12 Appert and canning equipment, designed and engraved by Henry Cheffer (1880–1957), and issued as a stamp by France on March 5, 1955. Source: www.stampboards.com/viewtopic.php?f=65&t=40366.



Figure 13 Early tinned can of roast veal taken on Parry's voyage to the Arctic in 1824. Source: www.cancentral.com/can-stats/history-of-the-can.

ranged from 2 to 9 kg in weight. The oldest survivor can be found in the Science Museum in London, measuring 14 cm high and 18 cm wide, and weighing a hefty 3 kg when filled (Geoghegan, 2013) (Fig. 14).

In 1824 Rear-Admiral Sir William Edward Parry took canned beef and pea soup with him on his voyage to the Arctic in HMS *Fury* during his search for the then elusive Northwest Passage to India. In 1829, Admiral Sir James Ross also took canned food to the Arctic, as did Sir John Franklin in 1845. Some of his food stores were found by the search expedition led by Captain (later Admiral Sir) Leopold McClintock in 1857. One of these cans was opened in 1939, and was edible and nutritious, although it was not analyzed for lead contamination from the solder used in its manufacture.

To complete the historical record, William Underwood left London and arrived in New Orleans in 1817. He traveled up to Boston where he started a business preserving food in glass jars using Appert's method. In 1819, Thomas Kensett, an engraver from England, started a similar business in preserved foods in New York in partnership with his father-in-law Ezra Daggett. The first offering of preserved provisions in tin cans in America is assumed to be the announcement by Daggett and Kensett in the *New York Evening Post* of July 18, 1822 (Bishop, 1978), although it was not until 1825 that they took out a patent (US 4,009X) in which 'vessels of tin' were mentioned. Daggett stepped down as Kensett's partner in February 1825, just after they had obtained the patent. Kensett briefly adopted the company name Thomas Kensett & Co., but the business seems not to have prospered. By 1829, when he died, he was describing himself in trade directories as an engraver, and not mentioning the canning company.

Tinplating

The traditional method for tinplating involved dipping or passing the steel through a bath of pure molten tin, but, since the 1930s, the process of depositing tin by electroplating has been used. The introduction of the electroplating process enabled a different thickness of tin to be applied to the two surfaces of the steel. This "differential tinplate" is of economic benefit to the user because it enables the most cost-effective coating to be selected to withstand the different conditions of the interior and exterior of the container.

The production of electrolytic chromium/chromium-oxide-coated low-carbon steel sheet (to give ECCS its full name) is very similar to electroplating, the only essential differences being that, in the case of ECCS, flow melting and chemical passivation are not involved. The initial development work was carried out in Japan in the 1960s when tin was on occasions in short supply,



Figure 14 Early tinned cans. Source: Science Museum, London.

and the price extremely variable. The thickness of the chromium coating is substantially less than the thickness of tin necessary to achieve the same corrosion protection for the underlying steel.

Retorting

The process to destroy the microorganisms present in the food at the time of closing of the container is now known as retorting. It confers commercial sterility which differs from total sterility in that some microorganisms may survive the heat treatment, but because of the conditions that exist inside the container (e.g. absence of substances essential for growth), they do not grow or spoil the food. A retort, also known as an autoclave or pressure cooker, is a pressure chamber used to carry out industrial processes requiring elevated temperature and pressure.

Appert used boiling water baths with residence times of several hours. The first mention made of an autoclave in the food literature is in the fourth edition of Appert's book in 1831. Chapter 8 was devoted entirely to the subject of autoclaves and their method of operation.

As early as 1808 Sir Humphry Davy, the eminent English chemist, had found that when calcium chloride was added to boiling water its temperature could be increased to 115 °C or higher. Isaac Solomon, the manager of a tomato canning plant in Baltimore is credited with applying this discovery to the processing of canned goods in 1861. He introduced a new procedure for heating containers to a higher temperature, thus reducing the sterilization period from five or 6 h to under an hour. Solomon's discovery led to higher production levels and lower prices, as factory output jumped from two to three thousand cans a day to twenty thousand cans. Solomon's innovation coincided with the beginning of the Civil War, which transformed the market for canned goods. Output rose from 5 million cans in 1860 to 30 million cans in 1865, a 600% increase.

In the Foreword to the classic book *Sterilization in Food Technology* (Ball and Olson, 1957), Laurence V. Burton relates the human interest tale of the strange breed of men who called themselves 'Processors' back in the period of about 1865 to 1890. They went from plant to plant during the canning season, often wearing stovepipe hats and commanding what was considered to be a fabulous salary in those days of \$0.10 an hour for common labor. All of them had one trait in common - secrecy. They worked behind locked doors, where not even the owner of the factory was permitted to enter and took charge of processing the cans of food in a calcium chloride bath. That the industry survived their uninformed ministrations is a tribute to both the strength of the cans and the fortitude of the pioneer canners of that day.

After Nicholas Appert's death in 1841, his nephew Prieur Appert managed the business until Raymond Chevallier-Appert (1801–92) came into possession of the business in 1846. Despite the similarity of the name, Chevallier-Appert was not related to Nicholas Appert (Goldblith, 1972). To avoid spoilage problems which occurred from time to time, Chevallier-Appert decided that higher temperatures were needed in cooking. He equipped an autoclave with a manometer to provide precise temperature control and patented the invention in 1852. The first industrial application of this autoclave took place in 1853 in the factory of the House Chevallier-Appert. However, as Goldblith noted, it is curious that no mention of this was made in the sixth edition of Appert's book edited by Prieur Appert and published in 1857. In the Belgian version of the sixth edition quoted by Goldblith, the water bath is still described as the means of providing sufficient heat to remove the occluded air in the jars or cans of conserves. Processing times of 1–2 hours were recommended for several products, in either a covered or an open water bath. The only mention of the autoclave was for the purpose of extracting gelatin from bones.

In 1841, Stephen Goldner who had been born in Hungary in 1810, filed a patent in the same year for the use of brine rather than water as the boiling agent, thereby increasing cooking temperatures - two years after the same patent in France.

Although the autoclave was adapted to canning in 1853 in France by Chevallier-Appert, it was apparently not known in the US. According to Bitting (1916), two - unsuccessful - US patents for a retort preceded that of Shriver. Patent US 51,164, dated November 28, 1865, by Samuel Sheldon Fitch from New York, for an 'Improvement in Apparatus for Cooking, Washing, and Bleaching' was for a vertical retort in which water was placed in the lower portion and the cans were either submerged in the water or surrounded by steam. US patent 89,419, issued in 1869 to Lewis McLellan from Gorham in Maine, for an 'Improvement in Cooking Canned Corn' was the first retort specifically designed for canning. The cans were set in racks and lowered through an opening at the top.

Andrew K. Shriver, a Baltimore canner, was awarded US patent 149,256 in 1874 for an Improved Apparatus for Preserving Hermetically-Sealed Cans of Fruit, Vegetables, Meats, &c. It consisted of a closed kettle in which processing was done with live steam or superheated water. He was aware that the idea of "subjecting the sealed cans and their contents to steam heat above 212° Fahrenheit is not new and I therefore do not claim such invention," but his kettle apparatus and process control mechanisms were unique. Shriver described the contemporary practice in his day: "Heretofore the can, after being filled, has been boiled in ordinary water, or placed in a bath of salt-water, in which a temperature of 230° is attainable, or in a chloride of calcium, whereby about 245° may be secured". Although Shriver's patent antedated Chevallier-Appert's French patent by 22 years, in all probability (in the opinion of a Professor of Food Science at Massachusetts Institute of Technology) Shriver had never heard of Chevallier-Appert's patent (Goldblith, 1972). However, it is highly likely that he was aware of the patents of Fitch and McLellan. By establishing consistent and measurable cooking times and temperatures for the wide range of foods being canned, the retort provided faster and more uniform sterilization.

Sanitary Can & Double Seam

The American Civil War (1861–65) provided the opportunity for canning to become a great industry in the US, and by the end of the war, canners had increased their output six-fold. For many years, the cans were made slowly and laboriously by hand. Both ends

were soldered to the can with a hole of about 25 mm in diameter left in the top. After the can was filled through this hole, a metal disc was soldered into place.

The growing market for canned foods provided the opportunity for Edwin Norton, co-owner of the can-making company Norton Brothers of Chicago, to invent the machinery for mass-producing cans. He began to patent new canister designs and the machines to make them, one operation at a time. By 1881 he held over 25 patents and by 1883 had successfully installed the first fully automatic can-making line. Norton went on to integrate on a massive scale. In 1901 he and the "tinplate trust" orchestrated a merger with 60 other firms (collectively with 95 factories) to form the American Can Company (ACC) with Norton as its first president. The following year he sold out to the "tin can trust" to form the rival Continental Can. Norton built an empire on his inventions and there are over 239 patents in his name covering machines for rolling, heating and coating tinplate, can designs, can-making, filling, closing, and testing (Twede, 2012).

Mechanization of the can-making process was made possible by the development of mechanical roll crimping (commonly known as double seaming) of the can ends onto a body with a soldered side seam. In 1896 Max Ams of New York received US patent 570591 for 'an improved construction of the seam between the can-body and the cover' making it possible to develop high-speed equipment for the making, filling and closing of these cans (Thorne, 1986). Known by several names including 'open-top can', 'The Ams Can' or most commonly 'the sanitary can', this novel invention had its technological roots in an old tinsmiths' technique known as double seaming. The double seam was a method by which tinsmiths joined two pieces of metal together without the use of solder. Each piece of metal had its edges rolled to form hooks, also referred to as flanges or curls. The hooks of each piece were rolled together forming a seam that consisted of five layers of metal. This method of creating a seam was used on a variety of tinware. In Europe during the late 19th century, tinsmiths began double seaming certain food cans, but they were unsuccessful using this method for "processed" foods, or tin cans subjected to hot water and steam pressure. The reason for their failure was the lack of a sealant to fill the spaces between the layers of metal in a double seamed can. Under heat or pressure, the product inside the can would leak at the seams (Pearson, 2016).

Max Ams and his son Charles developed a paper gasket which proved insufficient to seal the can. In 1896 Charles developed a rubber gasket from rubber dissolved in a solution of ammonia and water. In 1897, Ams hired engineer Julius Brenzinger to develop machinery for lining ends, drying them, and double seaming the ends onto cans. The commercialization of the Ams Sanitary Can depended upon the efforts of William Bogle, a wholesale distributor of canned goods from various canners in New York and Pennsylvania, and George Cobb of the Cobb Preserving Company in Fairport, New York. The Cobb Preserving Company spent many frustrating years attempting to pack food using the new cans and were finally able to can all their food products using the Ams Sanitary Can in late 1903. With Bogle's financial backing and organizational skills, Ams, Bogle, and Cobb combined their interests and formed the Sanitary Can Company in 1904, an entity that existed for only a few years before being purchased by the fledgling ACC in 1908. ACC, by then the leading manufacturer of cans in America, used their market leverage and applied engineering skills to fully promote the sanitary can over the next two decades. By the early 1920s, the sanitary can was nearly universally used throughout the canning industry, with the exception of condensed milk (Pearson, 2016). Unlike earlier containers, the sanitary can allowed companies to pack larger pieces of food with less damage. In addition, since a machine attached the lid, solder from the lid no longer came into contact with the food although solder from the side seam did (Fig. 15).

The sanitary can paved the way for automated can lines. Whereas before about 6 cans per hour were made, the first automated can lines could make about 60 cans per hour. Today, can-making lines can run as fast as 1500 cans per minute and can seamers can close over 1000 cans per minute.

An important innovation was the introduction of circumferential beads into the side walls of processed food cans to increase hoop strength and resistance to pressure demands during retorting.

Welded Side Seams

With the exception of some developing countries, very few food cans today are produced with soldered side seams, the concern of public health authorities being that lead from the tin/lead (2:98) solder would migrate into the food. Since the 1970s, most countries required that only pure tin solder be used on cans intended for baby foods, which added significantly to the cost of such cans. The use of tin/lead solder ceased when the US FDA issued a final rule in July 1995 prohibiting its use in food containers, including both domestic and imported food cans.

Welding, an alternative to soldering, had been considered for the side seams of cans for many years but because of inconsistencies in weld integrity, the process was considered unacceptable for the manufacture of high-quality leak-free cans. In the 1960s, two types of resistance welding processes gained commercial acceptance. Soudronic AG in Bergdietikon, Switzerland developed a wire weld system and sold side-seam welding machines worldwide from 1965. Robert W. Wolfe and Richard E. Carlson filed US patent 3,834,010 for a Method for Forming Welded Seam Can Bodies in 1972 and assigned it to the Continental Can Co., originally a US-based canmaker but parts of the company were subsequently acquired by Crown, Cork & Seal and VAW Germany. Their Conoweld® process was commercialized but is no longer in use. The most commonly used process now is that developed by Soudronic AG although similar machines are made by Fael and Cevolani.

Resistance welding substantially replaced soldering during the 1970s, largely as a result of concerns over atmospheric lead in the workplace and as a means of eliminating lead from food cans. In developed countries, the majority of three-piece tinplate cans used for food have welded side seams with most made from tinplate although ECCS cans can be welded provided that chromium oxide is removed from the welding area.

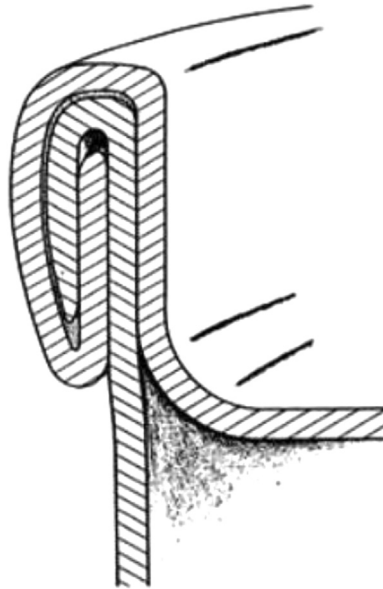


Figure 15 Cross-section of a double seam.

Cemented Side Seams

A system of chemical bonding of side seams was developed, mainly for dry or otherwise neutral products such as powders and oils. Driven by the ability to use cheaper materials, a number of companies developed alternative technologies for the manufacture of three-piece cans from ECCS. In the mid-1960s, the Mira seam can process was developed by the American Can Company in the US and the Toyo Seam Can process was developed independently by Toyo Seikan Kaisha Ltd. in Japan. They use a thermoplastic polyamide adhesive which is applied to one edge of the preheated body blank before it is rolled into a cylinder, providing complete protection of the raw edges of the blank. A strong bonded lap seam able to withstand the high in-can pressures generated by beers and carbonated soft drinks during exposure to warm temperatures or pasteurization was produced. Improvements in adhesive properties resulted in cemented side seam cans being able to withstand thermal processes up to 125 °C for 90 minutes (Matsubayashi, 1990). Since the advent of high-speed welding operations, the use of chemically bonded side seams has declined.

Can Opener

The Fortnum and Mason 1849 catalogue included instructions on how to open cans with a knife: “First stab a hole with the butt-end of the knife, near the upper rim of the canister; then insert the blade as far as it will go; draw the handle towards you (the claw resting against the canister as a lever), when the blade will be found to cut through the tin with perfect ease” (Geoghegan, 2013). However, it took several years before a satisfactory means of opening the cans developed. From the 1820s through the 1860s, soldiers in the field and sailors aboard ships used bayonets, knives, chisels, and even gunshots to get at their rations.

In 1855 a British maker of cutlery and surgical instruments, Robert Yeates, patented the first can opener consisting of a wooden handle and a claw-shaped blade that was pushed into the can end and then sawed around the edge. In 1858, another lever-type opener of a more complex shape was patented by Ezra Warner of Waterbury, Connecticut (US patent 19,063). It consisted of a sharp sickle which was pushed into the can and sawed around its edge. A guard kept the sickle from penetrating too far into the can. This opener was adopted by the US Army during the American Civil War. However, its unprotected knife-like sickle was too dangerous for domestic use but it found a home in many grocery stores where clerks would open cans for customers to take home. A plus to Warner’s design was that it consisted of several parts which could be replaced when worn out.

In 1870 another Connecticut inventor, William W. Lyman, received US patent 105,346 for a can opener with a wheel that allowed a smooth and continuous cut around the rim of a can. However, it was difficult to operate until a breakthrough came in 1925 when a second, serrated wheel was added by the Star Can Company of San Francisco to hold the cutting wheel on the rim of the can. The basic principle of this opener is the same as that used on modern can openers. An electric version of the same type of can opener was first sold in December of 1931 (Fig. 16).

The classic toothed-wheel crank design that is still used today was invented by Charles Arthur Bunker in 1926 who received US patent 1,838,525 in 1931. It featured the now standard pliers-type handles, that when squeezed would tightly grip the can rim, while turning the key would rotate the cutting wheel, progressively cutting the lid along the rim. Whereas all previous openers required using one hand or other means to hold the can, this opener simultaneously gripped the can and opened it. It remains the can opener standard to this day.

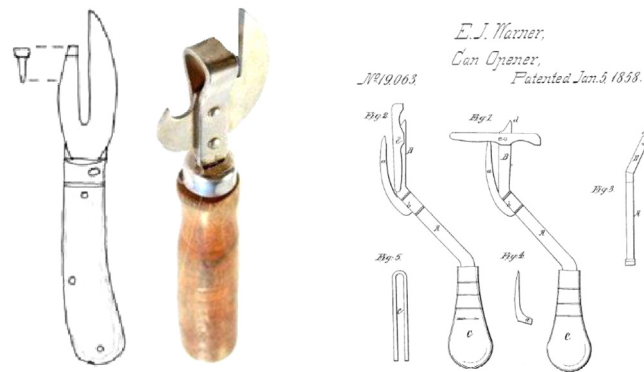


Figure 16 Lever-type can opener design by Robert Yeates in 1855 (left) and by Ezra Warner in 1858 (right).

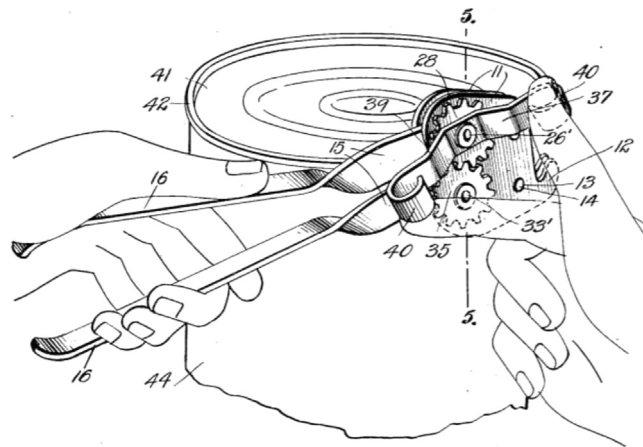


Figure 17 Classic toothed-wheel crank design can opener invented by Charles Arthur Bunker in 1926. From US patent 1,838,525.

A small can opener named the P-38 (so named for being 38 mm in length) was developed for the military in 1942 and issued in the canned field rations of the US Armed Forces from World War II to the 1980s. The simple tool could also double as a screwdriver. Though the US Armed Forces now eat MREs (Meals Ready-to-Eat) in flexible pouches that do not require openers, relief organizations still distribute P-38s along with canned food during disaster and rescue operations.

Easy-Open Can Ends

Several types of easy-opening devices, such as the key-opening scored strip found in solid meat or shallow fish cans, have been available for many years. However, increased demand for convenience features has seen the development of easy-open ends (EOEs) of two broad types: those which provide a pouring aperture for dispensing liquid products, and those that give a near full aperture opening for removing more solid products, making the can opener redundant. A pre-scored break line in the end, along with an affixed tab to break the score line and pull out the partial end, comprise the EOE.

Ermal Cleon Frazee of Dayton, Ohio established his own machine tool business (the Dayton Reliable Tool & Manufacturing Company) in 1949. He filed US patent 3,191,564 for a 'Method of fabricating a sheet metal joint' in 1963; the patent was issued in 1965 and he subsequently sold it to Alcoa who produced the first easy-opening or pull-tab ends. This followed earlier applications in 1961 and 1962 that were abandoned. Meanwhile, Justin Simpson and John S. Bozek of Chicago filed US patent 3,215,306 in 1964 for a pull tab; the patent was issued in 1965 and assigned to the Continental Can Company. Omar L. Brown and Don B. Peters of Dayton, Ohio filed US patent 3,349,949 in 1965 and assigned it to Frazee who was apparently their employer.

By 1965, around 75% of US breweries were using EOEs and they soon became widely adopted by canned beverage producers worldwide. However, because they were detachable, they resulted in litter and, in 1975, US patent 3,967,752 was granted to Daniel F. Cudzick from Reynolds Metals in Richmond, Virginia for a can end with an inseparable tear strip. This soon became the industry standard, and, in various formats, is known as the stay-on-tab (SOT) or colon tab. The end contains a scored region and a pull-tab that can be leveraged to open the hole by pushing the scored region into the can.

Most designs incorporate an EOE consisting of a scored portion in the end panel and a levering tab (formed separately) that is riveted onto a bubble-like structure fabricated during pressing. Most (but not all) of the entire aperture circumference is scored, leaving sufficient unscored portion to function as a hinge when the tab is pressed in to provide an opening in the can end.

In 1977 Jozef Tadeusz Franek and Peter Henry Doncaster of England were granted US patent 4,058,998 assigned to Metal Box Ltd. for a method of forming a neck and flange at the open end of a thin cylindrical one-piece metal can body. In the case of the beverage can, the most commonly-made body diameter is 65 mm which can be necked-down to diameters as low as 52 mm. This can be achieved in a variety of ways including spin-necking, die-necking and more recently roll-necking or a combination of processes. Multi-die necking, involving necking the can with smaller and smaller dies until the desired diameter has been reached, has proved very successful, as has the combined technique of die necking followed by a spin necking process. The diametral reduction results in an increase in metal thickness but, more importantly, allows the use of smaller diameter, resulting in considerable savings in material and cost.

A significant reduction in the amount of material required to make an aluminum end became commercial in 2001 when Crown Cork & Seal introduced the SuperEnd[®], achieving about a 10% decrease in weight while increasing the buckle failure strength of the end. Fig. 18 shows a comparison of profiles of the SuperEnd[®] and the older designs. The innovative ends utilize a unique angled chuck-wall design, which significantly reduces metal use and improves end performance. This unique design provides 20% more finger access to lift the opening tab, thus making it easier to open, and has become an industry standard for beverage ends (Robertson, 2013). To date, more than 500 billion SuperEnd[®] beverage ends have been produced by Crown and its licensees, saving over 130,000 metric tons of aluminum, 2200 metric tons of coatings and 1,000,000 metric tons of greenhouse gases (www.crowncork.com/beverage-packaging/innovations-beverage-cans/superend-beverage-ends) (Fig. 18).

Another end innovation is Crown's 360 End[®] where the entire end is removed, turning the metal can itself into a drinking cup and eliminating the need for separate glassware. Originally debuted in 2010 during the FIFA World Cup in South Africa, it is now used on beverage cans around the globe (Fig. 19).

Aluminum

Historical Development

Aluminum is the earth's most abundant metallic constituent, comprising 8.8% of the earth's crust, and is found in nature most commonly as bauxite that must be purified before it can be refined to aluminum. The Bayer process (invented in 1887 by an Austrian chemist Carl Joseph Bayer in St. Petersburg, Russia) is the principal industrial means of refining bauxite to produce alumina (Al_2O_3). Hans Christian Oersted, a Danish physicist and chemist, first isolated aluminum in 1825 using a chemical process involving potassium amalgam. Between 1827 and 1845, Friedrich Wöhler, a German chemist, improved Oersted's process by using metallic potassium. In 1854, French chemist Henri-Étienne Sainte-Claire Deville obtained the metal by reducing aluminum chloride with sodium. Aided by the financial backing of French emperor Napoleon III, Deville established a large-scale experimental plant and displayed 12 small ingots of pure aluminum at the Exposition Universelle of 1855 in Paris, where it was considered a precious metal (more valuable than gold or platinum) and was used mainly for jewelry. Almost immediately after the exhibition, demand for this magical metal sky-rocketed. The apex of the Washington Monument is capped by an aluminum pyramid 22.6 cm

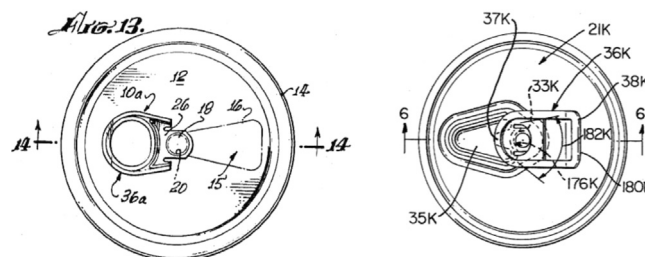


Figure 18 Pull-tab end from the 1967 Brown and Peters US patent 3,349,949 assigned to Frazee (left), and the 1976 Cudzik US patent 3,967,752 (right).

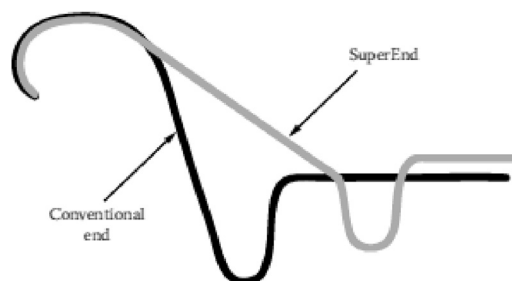


Figure 19 Cross-section of the end profile of a conventional end and a SuperEnd[®].

in height, 13.9 cm at its base, and weighing 2.85 kg making it, at the time of construction (1884), the largest single block of aluminum ever cast; its function was to serve as a lightning rod for the structure.

The Hall-Héroult process for the electrolytic reduction of alumina was invented independently and almost simultaneously in 1886 by the American chemist Charles Martin Hall and by the Frenchman Paul Lois Toussaint Héroult – both only 22 years old. They discovered that alumina would dissolve in fused cryolite (Na_3AlF_6) and could then be decomposed electrolytically to a crude molten metal. A low-cost technique (the Hall-Héroult process) is currently the only method used for the commercial production of aluminum, although new methods are under study. In 1888, Hall opened the first large-scale aluminum production plant in Pittsburgh that later became the Alcoa corporation which today is the eighth largest producer of aluminum. The Hall-Héroult process caused the price of aluminum to plummet from over \$1200/kg to less than \$1/kg at the start of the 20th century; the current price is less than \$2/kg. In only a couple of years, aluminum went from being a rare and precious metal, to one available in abundance because of a technological breakthrough (Frank et al., 2000).

Owing to the chemical stability of its oxides, the energy requirements for smelting are extremely high. This has led to the production of aluminum in areas where cheap electrical power is available. Most commercial uses of aluminum require special properties that pure metal cannot provide. Therefore, alloying agents are added to impart strength, improve formability and malleability characteristics and influence corrosion characteristics. A wide range of aluminum alloys is commercially available for packaging applications, depending on the container design and fabrication method used. Typical alloying elements include silicon, iron, copper, manganese, magnesium, chromium, zinc and titanium.

Compared with tinplate and ECCS, aluminum is a lighter, weaker but more ductile material that cannot be soldered. The reduction in metal thickness of the can body has continued incrementally over the past 70 years, at times facilitated by alloy development but mostly through optimization of can design and continues today in many parts of the world. It is estimated that close to 20% of the available aluminum worldwide is used for can making, particularly for beverage cans. Additionally, its use in flexible packaging, from aluminum trays to a variety of foils to metallization is quite common in food packaging.

There has been considerable concern about the potential role of aluminum in causing Alzheimer's disease (AD). The currently known genetic components of AD only partly account for all cases, and this suggests that other risk factors, such as environmental exposure, could be involved in the etiology of the disease. Some studies have reported high concentrations of aluminum in the AD brain, while others have not. A number of epidemiological studies have reported a positive association between the prevalence of AD and aluminum levels in drinking water, while other studies have not, and therefore its role in the pathogenesis of AD remains controversial (Frank et al., 2012). A recent paper is more unequivocal (Exley, 2017), claiming that aluminum acts as a catalyst for an earlier onset of AD in individuals with or without concomitant predispositions, genetic or otherwise. AD, according to Exley (Exley, 2017) is not an inevitable consequence of aging in the absence of a brain burden of aluminum. Hence, aluminum in direct contact to or exposure to food remains a concern.

Aluminum Foil

Aluminum foil is a thin-rolled sheet of alloyed aluminum varying in thickness from about 4–150 μm . It was first produced commercially in the US in 1913 where it was used for wrapping Life Savers™, candy bars and chewing gum. In 1921, it was laminated on paperboard to produce coated folding cartons. Household foil was marketed in the late 1920s, and the first heat-sealable foil was developed in 1938. Formed or semirigid containers appeared on the market in 1949. Today foil has been replaced in many applications by metalized films.

Aluminum Bottle

The aluminum beverage bottle (also referred to as a bottle can) was launched by Sapporo Breweries of Tokyo in 2000; it was developed and manufactured by Daiwa Can, Tokyo, Japan. A similar bottle was launched in the US for energy drinks in 2001. The bottles are made by either an impact extrusion (IE) or, since 2008, a Coil-to-Can (C2C) process, resulting in a wide range of shapes and sizes. A variety of standard finishes are available including a 26 mm standard crown cap, 38 mm lug finish, 38 mm continuous thread with a plastic sleeve, 38 mm ROPP and 28 mm continuous thread roll-on pilfer-proof cap.

Two-Piece Can Manufacture

A major innovation in can making was the introduction of the seamless or two-piece aluminum can in the 1950s and tinplate can in the 1970s. For many years, can makers manufactured by single pressing a shallow-drawn two-piece container such as the familiar oval fish can. However, the technology to produce deep-drawn cans is a more recent innovation, although the basic concept dates back to the Kellver system for producing cartridge cases developed in Switzerland during World War II.

There are two main methods used commercially to make two-piece cans: the drawn and ironed (D&I) process, which can be adapted to produce a can for pressure packs (including carbonated beverages) and for food containers, and the draw-redraw (DRD) process, which is a multistage operation and produces a can mainly suitable for food products and not beverages.

The first aluminum D&I cans were introduced in the US by two breweries in 1958: Prima in Hawaii and Coors in Colorado. However, it was not until 1971 that the first tinplate D&I can was launched. By comparison, the first three-piece soldered tinplate can for beer was introduced by the Kruger Brewing Company in the US in 1935 (Maxwell, 1993).

Two-piece cans have technical, economic and aesthetic advantages in comparison with soldered or welded three-piece cans. In terms of integrity, the two-piece can has no side seam and only one double seam, which is more easily formed and controlled because of the absence of a side seam lap juncture. The internal enamel/lacquer does not have to protect a soldered side seam or weld cut edge, and there are material savings in solder and (in the case of D&I cans) plate, the latter being up to 35% lighter than a standard three-piece can. Since 1970, through the conversion of three-to two-piece cans and subsequent lightweighting, the weight of a 350 mL tinplate beverage can has been reduced by more than 50%, and that of the inherently lighter two-piece aluminum can by over 40%. The technology exists to continue this trend, especially with tinplate cans. Finally, the absence of a side seam permits all-round decoration of the outside of the can, increasing the effective printing area and leading to a more aesthetically pleasing appearance.

The TULC (Toyo Ultimate Can) is a two-piece can that was developed by Toyo Seikan Kaisha in Japan in 1991. ECCS, laminated with PET film on the interior and exterior surfaces, is processed into cups, similar to how D&I cans are processed. It is then drawn, stretched and ironed to reduce the thickness of the side walls as the container height increases. However, unlike D&I cans, no coolant (lubricant) is used during the forming process, thus eliminating the need for coolant rinsing and wastewater treatment. Due to the internal layer of PET, no internal enamel/lacquer coating is required, resulting in a significant reduction in CO₂ emissions, a by-product of the internal enamel/lacquer curing process. In Japan, TULC has achieved a 20% market share but limited uptake elsewhere. More recently, a PET-laminated aluminum two-piece can known as aTULC has been developed; it is manufactured by the direct coating of an aluminum sheet with molten resin (Robertson, 2013).

Aerosols

The present aerosol industry is generally considered to have received its stimulus from the development of aerosol insecticides used in World War II, although a few aerosols had been marketed prior to this time. The concept of an aerosol originated as early as 1790 when self-pressurized carbonated beverages were introduced in France. Metal spray cans constructed from heavy steel were being tested as early as 1862 but they were too bulky to be commercially successful. In 1882 the use of compressed gases for charging of milk products was patented and in 1896 US patent 88,348 was granted to Peter H. Vander Weyde and John Matthews from New York covering the use of nitrous oxide in artificially aerated drinks.

Erik Andreas Rotheim, a Norwegian chemical engineer and inventor, submitted a patent application in 1926 for an aerosol spray can and valve that could dispense different fluids using dimethyl ether as a propellant. The Norwegian patent was granted in 1929. Rotheim filed a patent application in 1927 for a 'Method and means for the atomizing or distribution of liquid or semiliquid materials' and was granted US patent 1,800,156 in 1931; he then sold the patent rights to a US company for 100,000 Norwegian kroner. In 1998, the Norwegian post office issued a stamp celebrating the Norwegian invention of the spray can.

After World War II, people began looking for new ways to use the aerosol package developed during the war for dispensing insect repellent. In 1946, the Crown Cork & Seal Company introduced the first seamless, lined and lithographed aerosol canister - the Spratainer.

Aaron S. (Bunny) Lapin from St. Louis, Missouri, founder of Clayton Corporation, introduced the patented Reddi-Wip[®] nitrous oxide-propelled, sweetened whipped cream with fluting to create a pattern and a tilt-to-open design that preserved the propellant in 1947. Besides packaging Reddi-Wip[®], the Clayton Corporation also made and sold its own valves. By the time he received US patent 2,704,172 for 'Dispensing valves for gas pressure containers' in 1955, the invention had already helped make him a millionaire. Time magazine in 1998 selected Reddi-Wip[®] in its cream-of-the-crop roundup of the 20th century's top 100 consumer items, alongside color TV, the home dishwasher, the paper clip, the pop-top can and Spam (the food, of course). Reddi-Wip[®] is now produced by ConAgra Foods.

In 1949 Rich Products Corporation in Buffalo, New York launched Rich's Whip Topping made from isolated soy protein in a Spratainer aerosol can. By the mid-1950s a range of food aerosol products were on the market, including a drink mix, barbecue sauce, chocolate and table syrups, a vitamin syrup, a meat tenderizer and a salad dressing. Unfortunately, several of these products were disappointing and development work on new aerosol products dwindled almost to a stop. Nabisco introduced processed cheese under the name Snack Mate in 1966, and in the late 1970s Pillsbury introduced a viscous decorative icing in an aerosol can.

Modern aerosol spray products have three major parts: the can, the valve and the actuator or button. The can is most commonly two- or three-piece enameled/lacquered tinplate; aluminum cans are also common for more expensive products or products intended to have a more premium appearance. The 'crimp-on valve' used to control the spray in low-pressure aerosols was developed in 1949 by Bronx machine shop proprietor Robert H. Abplanalp who received US patent 2,631,814 for a 'Valve mechanism for dispensing gases and liquids under pressure' in 1953.

The Advanced Barrier System[®] (ABS) bag-in-can system from CCL Container separates the product from the pressurizing agent with a hermetically sealed, multi-layered laminated pouch. The pouch maintains total formulation integrity and freshness and extends shelf life. Aluminum containers with the ABS system conform to FDA requirements for most food products. The CCL Container piston barrier package assures separation of the product from the propellant and is often selected for highly viscous products such as food spreads. The main benefit of this system is that it eliminates gas permeation.

Propellants available for food use include N_2O , CO_2 and N_2 . Freon C-318 and Freon 115 were approved in the 1960s by the US FDA for use in food aerosols but concern in the mid-1970s over the use of fluorocarbons adversely affecting the ozone layer and the signing of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987 led to their substitution with the water-soluble hydrocarbons butane, isobutane and propane.

In terms of the total worldwide aerosol market of over 15 billion units annually (Niemiec et al., 2018), the food aerosol market is very small. However, it is an area that does have significant growth potential. The major applications by volume at the present time appear to be whipped cream, cheese spreads and pan release sprays (i.e. edible cooking lubricants).

Protective Coatings for Metal Containers

The use of organic coatings is widely used in the production of metal food containers to protect the metal from corrosion by the contents and/or to protect the contents from being contaminated by dissolved metal from the can, thus preventing color, odor and flavor degradation and possible ill-health. Several can-coating resin types are commercially available, including natural oleoresinous compounds and synthetic resins (acrylic, epoxy, phenolic, polyester and vinyl resins). Each resin can be produced from multiple starting materials (natural substances or monomers) and the final polymer is typically blended to achieve the desired attributes suited for each can/filling combination (Ellis, 1979). Synthetic resins solidify in a manner similar to plant resins but are liquid monomers of plastics that cure irreversibly.

Early organic can coatings were based on oleoresinous products, made by fusing natural gums and rosins and blending them with drying oils such as linseed or tung oil (also known as China wood oil) a drying oil obtained by pressing the seed from the nut of the tung tree (*Vernicia fordii*). Oleoresinous systems are still used today because of their low cost and good acid resistance. However, the open micellar structure of oleoresinous materials makes them prone to corrosion/staining problems with sulfur-bearing products unless they are pigmented with zinc oxide paste. It was for this reason that a departure was made from these naturally-occurring raw materials to synthetic phenolic resins dissolved in a blend of solvents (Good, 1988). Synthetic resins, developed beginning in the 1940s, provided more flexibility in meeting technological requirements for high-speed manufacturing and for contact with varying foods and drinks (Ellis, 1979).

In 1909, the Russian chemist Nikolaus Prileschajew reported in a German chemistry journal the chemical reaction of an alkene with peroxybenzoic acid to form epoxides. Peroxy acid epoxidations currently play an important role in epoxy resin production. In 1934, Schlack of I. G. Farbenindustrie AG in Germany applied for a patent and in 1938 received US patent 2,136,928 describing the preparation of high-molecular-weight polyamines by the reaction of amines with epoxide compounds containing more than one epoxide group. Among the various materials was a product prepared from epichlorohydrin and bisphenol A. It was disclosed that this resin could be hardened with equivalent amounts of amine. However, Schlack and/or Farben failed to recognize the significance of the latter part of this invention. The realization of the true value of these products came a few years later. Almost simultaneously and independently, two inventors, Pierre Castan of De Trey Freres in Switzerland and Sylvan Owen Greenlee in the US, recognized the value of epoxy resins as we know them today (Tess, 1987). Castan received US patent 2,324,483 in 1943 for a 'Process for preparing synthetic resins' and licensed it to Ciba AG of Basel, Switzerland (now Novartis International AG) and in 1946, the first epoxy adhesive was shown at the Swiss Industries Fair. Greenlee received US patent 2,456,408 in 1948 for 'Synthetic drying compositions' with the patent assigned to the Devoe-Raynolds Company (later Celanese Chemical Company) in Louisville, Kentucky. Around 1947, epoxy resins were commercially introduced into the market.

In the late 1940s, Shell Chemical Company, the only supplier of epichlorohydrin at that time, and Union Carbide (then Bakelite) entered the field of epoxy resins. In the summer of 1955, the four basic epoxy resin manufacturers entered into a cross-licensing agreement. Subsequently, Dow Chemical Company and Reichhold Chemicals entered the patent pool and introduced commercial lines of epoxy resins. Compared to the oleoresins that preceded the use of epoxies, epoxy resins provided substantially greater flexibility (Gannon, 1986).

The use of thinner gauge steel with reduced tin coating weight in the 1960s placed greater emphasis on more sophisticated organic film formers. Phenolic resins produced by the condensation of one or more phenols with one or more aldehydes were introduced in 1961 by Shell Chemical Company, and although they are highly corrosion-resistant, they have limited uses due to their poor flexibility. In 1978, the use of polyester-urethanes for internal coatings began.

In the past, most coatings used in can manufacturing contained a high concentration of solvents, resulting in significant emissions of volatile organic compounds (VOC's). However, in the 1970s, clean air regulations created a demand for coatings with lower VOC content, which led to the development of alternative can coating formulations and technologies such as waterborne, UV-cured, and powder coatings.

The epoxy resins are produced by condensation of epichlorohydrin and bisphenol A (BPA), yielding bisphenol A diglycidyl ethers (Robertson, 2013). At present, epoxy-based resins account for up to 95% of the polymers for coating aluminum and steel cans. They have attracted attention in recent years because their foundational building block is BPA. Widespread human exposure to BPA, as well as BPA's potential health effects, have been the subject of intense scientific and public scrutiny and debate.

The first evidence for the toxicological properties of BPA was published in the 1990s and the debate on the safety of BPA intensified in the early 2000s. In 2015, the use of BPA-based coatings in food and beverage cans was banned in France (LOI no 2010-729) and in 2016, the US food companies Del Monte and Campbell announced the phase-out of BPA-based coatings by 2016 and 2017

at the latest, respectively. In July 2019, the General Court of the European Union announced “confirmation of the inclusion of Bisphenol A as a substance of very high concern on account of its properties as a substance toxic for reproduction”.

Although several alternative coatings already exist, none of them can be regarded as an ‘ideal’ can coating. During recent years, various biomass resources such as lignin, sugar, plant oil, isosorbide, rosin, itaconic acid, eugenol, and vanillin have been used to produce biobased epoxy resins (Kumar et al., 2017). Among them, low-cost, non-toxic, and abundant plant oils are suitable candidates for epoxy resin manufacture, including epoxidized sucrose ester of fatty acids, high oleic sunflower oil and tall oil fatty acids, a byproduct of the pulping industry. A recent review provides further details (Mustapha et al., 2019).

Retort Pouch

Developed in the 1950s, the retort pouch is a flexible package (pouch, tray, dish, bowl, or cup) that is used in place of the cylindrical metal can or glass jar. A flexible pouch is the most common manifestation, being hermetically sealed on three or four sides and made from one or more layers of plastic or foil, each layer having a specific functionality. The choice of barrier layers, sealant layers and food contact layers depends on the processing conditions, product application and desired shelf life. Typical processing conditions involve temperatures of 121 °C for up to 30 min or 60 min for the large (3.5 kg) catering packs.

Thermally processed foods in flexible packaging (often known as retort pouches) may be compared with foods packed in metal cans, although the outward appearance of the flat pouch and the convenience of reheating by immersion in hot water invites comparison with frozen ‘boil-in-bag’ foods. One of the attractions of the retort pouch compared to the metal can is the thin profile of the package (12–33 mm for 200–1000 g pouches), enabling retorting times to be reduced by up to 60%, final quality to be improved, as well as rapid reheating prior to consumption. Other advantages include the ease of carrying, reheating and serving, as well as weight and space-saving. Finally, disposal of the used pouch is much simpler than for the metal can as it can be easily flattened. It is for all of these reasons that retort pouches have found wide acceptance by military forces, the US military term for this type of package being “Meal, Ready-To-Eat” (MRE) (Al-Baali and Farid, 2006; De Salcedo, 2015).

Development of the retort pouch in the US ranged from lab work in the early 1950s to use in the Apollo space program beginning in 1968 to the demonstration of commercial feasibility in 1968–72. The earliest recorded studies in the US using flexible packaging materials for thermally processed foods are those reported by Hu et al. (1955) and Nelson et al. (1956) at the University of Illinois, although Gould et al. (1962) stated that the idea was proposed as early as 1940 (Lampi, 1977).

In the 1950s, the US Quartermaster Food and Container Institute for the Armed Forces (predecessor of the US Army Natick R&D Command) saw the potential of retort pouches from a functional aspect for combat rations. In addition to carrying out internal studies, the Quartermaster supported exploratory contract work to get answers to fundamental questions. For example, Massachusetts Institute of Technology researchers Proctor and Nickerson (1958) studied a variety of materials for resistance to bacterial penetration including the PET/aluminum foil/PVC material preferred at that time for retort pouches. From 1959 to 1966, Natick screened more than 200 materials to be used in the manufacturing of pouches (Al-Baali and Farid, 2006). Films were bonded to the aluminum foil by an isocyanate adhesive system but the migration of traces (0.3 to 3.0 parts per billion) of toluene diisocyanate (TDI), one of the reactants necessary for the adhesive, into food-simulating solvents in the mid-1970s led to the development of extrusion lamination as a bonding technique (Lampi, 2009).

Wallenberg and Jarnhall (1957) from Åkerlund & Rausing in Sweden also surveyed a variety of films, concluding that the concept was feasible but cautioned that air must be evacuated prior to sterilization to preclude bursting of the pouch. Nughes et al. (1973) revealed that Star Stabilimento Alimentare S.p.A. in Milan, Italy initiated limited production of retort pouches in 1960 and had expanded ever since. In January 1971, Giovanni Nughes received US patent 3,556,816 (filed in October 1968), assigned to Star, for a flexible package for food. The patent described a heat-sealed flexible-walled food container formed of laminated material comprising aluminum foil coated on both surfaces with polyester layers and an inner polypropylene layer bonded to one of the polyester layers, the aluminum foil and polyester layers preventing the formation of microscopic cracks in the aluminum resulting from thermal stresses during sterilization.

Continental Flexible Packaging, Chicago, IL, began work on retort pouch materials in 1958 and, in conjunction with Ohio State University, tested sample pouches under simulated retort conditions in 1959. In 1962 Continental’s pouch material was used in Natick’s first commercial procurement of 40,000 pouches (Al-Baali and Farid, 2006). Continental’s licensees began using Continental’s material in Denmark and England in 1967, Japan in 1968, and Canada in 1975. Continental’s material was also used in Natick’s reliability project in 1968–72, the Apollo space program in 1969, and a hospital-feeding study in 1971.

Reynold’s flexible packaging division began working on the retort pouch concept in the mid-1950s, and in the early 1960s ran two trials in New York and Florida. In 1968 Reynolds successfully used roll stock pouch material in the commercial packaging of vegetables in pouches that were used for consumer testing (Al-Baali and Farid, 2006).

Meanwhile in Japan in 1963 the cook-in-pouch (CIP) was developed as a boilable pouch, and in 1964 a foil-free retortable pouch was developed featuring an outer layer of PET and an inner layer of HDPE laminated to the PET with an isocyanate-type adhesive. These pouches were used to pack hotchpotch and meat dumplings in 1967, marking the first and second retort foods in Japan (Yamaguchi, 1990). In February 1968, Otsuka Foods Co. in Japan launched Bon Curry in heat-resistant bags made of laminated plastic films. Although the first pouch curries had a shelf life of only two months, within a year they had developed a pouch consisting of layers of plastic and aluminum foil that offered a two-year shelf life. By 1973, Otsuka Foods was selling 100 million packs a year.

The retort pouch had become a commercial reality in the US by the end of the 1970s, and much of the credit is due to the three groups (Natick, Continental, and Reynolds) that were named as joint recipients of the 1978 IFT Food Technology Industrial Achievement Award (Mermelstein, 1978). NASA began using retort pouch food for space missions in the late 1960s and the US Army began delivering large quantities of MREs to troops in 1981 (Lampi, 1980, 2009; Barrett and Cardello, 2012; De Salcedo, 2015).

The structure of the retortable pouch used today is a laminate of three materials: an outer layer of 12 μm PET film for strength, an adhesive laminated to a middle layer of 9–18 μm aluminum foil as a moisture, light, and gas barrier, which is laminated to the inner layer of 76 μm polypropylene film as the heat seal and food-contact material. The use of PET film is to provide high-temperature resistance, toughness, and printability. Transparent retort pouches can be produced by replacing the aluminum foil layer with SiO_x -coated PET, thus allowing the pouch to be reheated in a microwave oven. MREs must be able to withstand more rigorous physical environments than consumer pouches and are currently packed in a quad-laminate pouch: an outer layer of 8 μm PET film, a 9 μm biaxially oriented nylon 6, a 5–11 μm aluminum foil layer and an inner layer of 46–62 μm polyolefin.

Jerome J. Landy was granted US patent 3,215,539 in 1965, and Forren E. Long, Fred B. Shaw and Harvey C. Lisle received US patent 3,261,140 in 1966 assigned to the Continental Can Company, Inc., New York for, respectively, techniques for batch and continuous sterilization of foods in flexible containers using microwave energy. Both procedures were limited to packages formed of nonreflective materials i.e., no aluminum foil. O'Meara et al. (1976) described a technique for using microwave energy to raise the temperature of foods in foil-free pouches from 200°F to 250–260°F in 1 minute with 2450 MHz microwaves.

The pressurized continuous microwave sterilization of food in pouches was patented in 1976 by Ernest M. Kenyon, Daniel Berkowitz, and John A. Ayoub and assigned to the US Army (US patent 3,961,569). Microwave-assisted thermal sterilization (MATS) technology of packaged foods such as MREs is built on the packaging and processing innovations of overpressure retorting using microwave-permeable flexible plastic containers. Current development of a 915 MHz MATS system shows promise for industrial and military applications. Large-scale processing systems designed by 915 Labs™ are now being offered commercially. For MATS processing, most high-barrier polymeric films currently used are multilayered with EVOH or SiO_x -coated-PET as a barrier layer (Zhang et al., 2018).

A blank-fed, retortable, square-shaped paperboard carton for soups, ready meals, vegetables and pet food was commercialized by Tetra Pak in 2003 as a replacement for the metal can and a competitor for the retort pouch; it is known as Tetra Recart®. Of basically similar structure to the Tetra Brik aseptic carton but with polypropylene replacing polyethylene, foods packaged in it have a shelf life under ambient conditions of 18 months.

Flexible Pouches

Barthélemy Thimonnier (1793–1857) was a French inventor who is attributed with the invention of the first sewing machine that replicated sewing by hand, receiving a patent in 1830. However, use of the machine did not spread due to strong opposition from tailors and Thimonnier's financial situation remained difficult; he died in poverty at the age of 63. The Thimonnier name lived on however, and in 1947 the company invented a high frequency sealing machine. Their move into food packaging began in 1957 when they released the original pillow pouch for packaging milk. Léon and Louis Doyen (the latter the CEO of Thimonnier) from Lyon, France were granted US patent 3,380,646 in 1968 (filed in 1963) for a stand-up pouch having a bottom gusset that expanded when filled so that it could stand up on shelves and tables. The trademark DOYPACK® (from DOYen PACKaging) was filed internationally and in 1965 the first machine for making and filling fruit juices into DOYPACK® pouches was launched; an aseptic packaging machine for UHT milk followed in 1972. The volume of the pouches offered varies from 50 to 5000 mL. The DOYPACK® pouches became extremely popular, driven by growth markets in India, Latin America and Africa.

In 1931, Rudolf Wild founded a company in Heidelberg, Germany specializing in food ingredients. In 1967 in collaboration with the Kalle and Thimonnier companies, Wild Flavors and Specialty Ingredients developed the Capri-Sun (named after the Italian island of Capri) stand-up pouch packaging system and launched it in Germany in 1969 as a 200 mL pouch. A reclosable twist-off cap was added in 2007. The Kraft Heinz Company manufactures and markets Capri Sun in North America.

Hosokawa Yoko Co., Ltd., Tokyo, Japan developed the Cheerpack™ pouch with attached spout and screw-cap suitable for non-carbonated liquid foods. It can be designed to hold volumes from 70 to 2000 mL and can be cold- or hot-filled as well as retorted or frozen. The Cheerpack™ pouch consists of four panels or sections – a front and back facing with two side gussets. The laminate construction consists of PET/Aluminum foil/PET/LDPE; or PET/EVOH/LDPE; or PET/Aluminum foil/PP/OPA (Tacchella, 1999). A HDPE neck and straw can be sealed into the top portion of the pouch. Gualapack S.p.A., Castellazzo Bormida, Italy was founded in 1984 and in 1987 became the global licensee for Cheerpack™. A strategic partnership established Cheer Pack North America in 2008 consisting of Hosokawa Yoko, Gualapack, and the US CDF Corp. and supplies the Cheerpack™ pouches and equipment for filling and capping them.

ICI in the UK developed a new container in the 1960s designed to offer an alternative to glass bottles and metal cans for beer and carbonated soft drinks. Known as the Merolite pouch, it consisted of a 3 g PVDC-coated PET film made into a tube supported by a 7 g cylinder of paper to hold 250 mL of beverage. The lid was opened by tearing off a strip of plastic covering a series of pouring holes. Although the technical achievements involved were significant, a filling rate of just 15/min (compared with contemporary canning line speeds of over 2000/min) meant that it could not compete without huge investment to develop faster machines. In addition to this, the public found it unattractive and inconvenient and there were problems associated with educating consumers

to accept the containers' novel appearance and handling characteristics. [Goddard \(1995\)](#) considered that it was too far ahead of its time but suggested that something like this, in an improved form, would reappear in the future; to date that future has not arrived.



Figure 20 DOYPACK® pouches (left) and Ecolean pouch (right).

In 1997 Ake Rosén from Helsingborg, Sweden was granted US patent 5,635,011 (filed in 1994) assigned to Tetra Laval Holdings & Finance S.A., Pully, Switzerland for a packaging film made of 40% calcium carbonate (to add stiffness and whiteness) blended with conventional PP and PE. Initially part of Tetra Pak, a new company Ecolean was established in 1996 in Helsingborg, Sweden. Although the combination of chalk and polymers was not entirely new (it can, for example, be found in cable insulation and car bumpers), it was unique in packaging. On average, the pouches are 50% to 60% lighter than conventional alternatives with a 1 L pouch weighing 14 g. In 2009 the Ecolean® Air Aseptic was introduced. The multilayer co-extruded film contains chalk and has extended light and oxygen barriers. Electron beam technology is used for package sterilization. Since the aseptic packaging material is completely aluminum free, the product can be heated in a microwave oven while still in the package. Recently the company has offered Ecolean Air Aseptic Clear, a transparent aseptic packaging for liquid food products.

Plastics Packaging

Historical Development

The adjective plastic is derived from the Greek *plastikos*, meaning easily shaped or deformed. It was first introduced into the English language in the 19th century to describe the behavior of the recently discovered cellulose nitrate that behaved like clay when mixed with solvents. Although the chemical nature of polymers (and the fact that they consist of enormous molecules) was not understood until well into the 20th century, the materials themselves, and the industry based on them, existed long before that ([Andrady and Neal, 2009](#)).

Baron Jöns Jacob Berzelius (1779–1848) was a Swedish chemist who coined the word polymer in 1833 just seven years after Michael Faraday had shown rubber to have the composition of C_5H_8 and six years before the discovery of the vulcanization process by Charles Goodyear. Berzelius also coined the terms isomer, catalyst and protein ([Seymour, 1989](#)). However, his original definitions differ dramatically from modern usage.

Since plastics include compounds obtained by chemical alteration of natural macromolecular compounds, then the earliest example of a plastics material would have to be hard rubber. Natural rubber was crosslinked or vulcanized by Liedershoff who heated it with sulfur in 1832. In 1838, Nathaniel Hayward from Woburn, Massachusetts patented the use of sulfur as an additive to decrease the tackiness of natural rubber. After purchasing this patent in 1839, Charles Goodyear, an American self-taught chemist and manufacturing engineer, accidentally allowed this patented mixture to remain overnight on a hot stove and obtained a more versatile product that retained its elasticity over a wider temperature range than the raw material and had greater resistance to solvents ([Seymour, 1989](#)). The rubber–sulfur reaction was termed ‘vulcanization’ by an English rubber manufacturer in honor of the Roman god of fire, and the product ‘Vulcanite’. The significance of the discovery of hard rubber lies in the fact that it was the first thermosetting plastics material to be prepared and also the first plastics material that involved a distinct chemical modification of a natural material.

It is generally considered that the development of the plastics industry began in the 1860s. At the International Exhibition of 1862 in London, Alexander Parkes, an English chemist and metallurgist, displayed a new material (which he later modestly called ‘Parkesine’) that he had made by treating cotton waste with a mixture of nitric and sulfuric acids. This was already a well-known process used for making the explosive called guncotton, but Parkes found that by altering the proportions and then mixing the resulting material with castor oil and camphor, the compound could be molded into decorative and useful articles. He was awarded a bronze medal for this invention at the Great International Exhibition in London in 1862, but unfortunately the Parkesine Company, which he formed in 1866 to commercialize his process, went bankrupt in less than 2 years. In 1869, a collaborator

of Parkes, Daniel Spill, formed the Xylonite Company to process materials similar to Parkesine. Once again, economic failure ensued and the company was wound up in 1874. Undaunted, Spill moved to a new site, established the Daniel Spill Company and continued production of Xylonite and Ivoride (Robertson, 2013).

In the 1860s, Phelan and Collander, a US firm manufacturing ivory billiard balls, offered a prize of \$10,000 for a satisfactory substitute for ivory because the decimation of elephant herds had resulted in an enormous increase in the price of ivory. In an attempt to win this prize, the US inventor John Wesley Hyatt solved the technical problems that beset Parkes by using camphor in place of castor oil. In 1870 a patent was issued to brothers John W. Hyatt and Isaiah S. Hyatt, of Albany, NY for Celluloid™, a mixture of pyroxylin (partly nitrated cellulose) and camphor produced at high temperature and pressure (US patent 105,338). This was the first commercially available plastic and the only one until the development of Bakelite by Baekeland in 1907. Although Hyatt did not win the prize, his product was used in the manufacture of objects ranging from dental plates to shirt collars. Despite its flammability and liability to deterioration in the presence of light, Celluloid™ achieved notable commercial success.

Other plastics were gradually introduced over the next few decades. Among them were the first purely synthetic plastics, the family of phenol–formaldehyde resins developed by the Belgian–American chemist Leo Hendrik Baekeland and sold under the trademark ‘Bakelite’. The first of his 119 patents on phenol–formaldehyde plastics was taken out in 1907 and US patent 1160362 entitled ‘Method of Making a Plastic Body’ was issued in 1915. Other plastics introduced during this period include modified natural polymers such as rayon made from cellulose.

The first hypothesis of the existence of macromolecules was advanced by the German organic chemist Friedrich August Kekulé (later Friedrich August Kekule von Stradonitz) in 1877 when he proposed that many natural organic substances consist of very long chains of molecules from which they derive their special properties. The step from the idea of macromolecules to the reality of producing them took the genius of the German organic chemist Hermann Staudinger, who in 1924 proposed linear structures for polystyrene (PS) and natural rubber. In 1920 he had hypothesized that plastics were truly giant molecules or, as he called them, ‘macromolecules’ (Kaufman, 1968). His subsequent efforts to prove this claim initiated an outburst of scientific investigation that resulted in major breakthroughs in the chemistry of plastics and the introduction of large numbers of new products such as cellulose acetate and poly(vinyl chloride) (PVC) in 1927 and urea–formaldehyde resins in 1929. Further developments occurred in the 1920s, but the years 1930–40 were probably the most important decade in the history of plastics as today’s major thermoplastics were developed. Further developments continue, with special purpose rather than general purpose materials having been developed in recent years.

The first Nobel Prize associated with macromolecules was awarded to British chemist Sir Walter Norman Haworth in 1937 for his investigations on carbohydrates and vitamin C. Hermann Staudinger was awarded the Nobel Prize for chemistry in 1953 for his efforts in establishing the new arena of polymer science.

Polyolefins

Olefin means oil-forming and was originally the name given to ethylene. Today polyolefin is a common term in the plastics industry and refers to the family of plastics based on ethylene and propylene. Polyolefins form an important class of thermoplastics and include very low-, low-, linear low-, medium- and high-density polyethylenes and polypropylene. Polyethylene was first synthesized by the German chemist Hans von Pechmann, who prepared it accidentally in 1898 while heating diazomethane; he called it polymethylene. The first industrially practical synthesis of polyethylene was discovered (again by accident) by Eric W. Fawcett and Reginald O. Gibson in 1933 at the Imperial Chemical Industries (ICI) Winnington facility in Northwich, England during a research program devoted to the effects of extremely high pressures on chain reactions. The basic patent relating to polymerization of ethylene was granted in 1937 (British patent 471,590) with full commercial-scale production commencing in 1939. For the first few years of its production, it was used in the electrical industry, particularly as an insulating material for underwater cables. By 1943, and with the support of the US Government, both Union Carbide Chemical and DuPont had licensed the ICI process and were starting up production facilities in North America.

In 1953, partially as a result of the post-war boom in catalyst development, two separate research groups on different continents discovered high-density polyethylene (HDPE) almost simultaneously. In the US, a group led by John P. Hogan and Robert L. Banks at Phillips Petroleum Company developed a chromium trioxide-based catalyst. At the Max Planck Institute in Mülheim, Germany, Karl Ziegler and Erhard Holzkamp were working on titanium-based catalysts. Both groups demonstrated the feasibility of producing almost completely linear HDPE at virtually the same time and in 1955 HDPE was produced as pipe (Dobbin, 2018). Ziegler was awarded the 1963 Nobel Prize for Chemistry.

From the late 1950s into the late 1960s, DuPont, Union Carbide Chemical and The Dow Chemical Company worked separately on developing copolymers of ethylene with α -olefins such as 1-butene, 1-hexene, and 1-octene. These linear copolymers are classified as linear low-density polyethylene (LLDPE) and have much better mechanical performance than LDPE. LLDPE was commercialized in 1977 and has penetrated almost all the traditional markets for polyethylene.

Substituted Olefins

Polystyrene (PS) was the first of the moldable clear rigid plastics to reach the commercial market in large volumes in the late 1940s. It could be rapidly molded into finished shapes because of its ease of flow in the melt and its fast-setting nature from the melt. New

applications of PS involve coextrusion with barrier resins such as EVOH and PVDC copolymer to produce thermoformed, wide-mouthed containers for shelf-stable food products and multilayer blow molded bottles.

Extruded PS foam sheet is a closed cell, 0.13 to 6.4 mm thick sheet made by a variety of extrusion processes. A large percentage of foam sheet is thermoformed using CO₂ as a blowing agent. Most PS foam sheet is used for disposable packages such as meat and produce trays, egg cartons, disposable dinnerware and containers for take-away or carry-out meals.

Polyvinyl Chloride

A range of polyvinyl chloride (PVC) films with widely varying properties can be obtained from the basic vinyl chloride monomer. Unplasticized PVC is a rigid sheet material that is thermoformed to produce a wide range of inserts from chocolate boxes to biscuit trays. Although PVC made extensive penetration into the market for a wide range of foods including fruit juices and edible oils, in recent years it has been increasingly replaced by PET. To a large extent, the properties of plasticized PVC film depend on the type of plasticizer used, as well as the quantity.

Polyvinylidene Chloride

Polyvinylidene chloride (PVDC) homopolymer yields a rather stiff film which is unsuitable for packaging purposes. However, when PVDC is copolymerized with 5% to 50% (but typically 20%) of vinyl chloride, a soft, tough and relatively impermeable film results. These copolymers were first marketed by Dow in 1939 under the trade name Saran[®]. It was accidentally discovered by laboratory worker Ralph Wiley and the name 'Saran' was coined by his boss Jack Reilly by combining the names of his wife Sarah Reilly and daughter Ann Reilly. Saran Wrap was introduced by Dow Chemicals in 1953 but in 2004 it was replaced by LLDPE due to environmental concerns about chlorine.

PVDC copolymers have the best combination of a high gas barrier and low moisture permeation of any commercial packaging plastic. They are frequently used as a thin layer between cellophane, paper and plastic packaging to improve barrier performance. The polymers can be solvent coated, extruded, thermoformed and readily form films. Their ability to provide packaging with a barrier against gases, odors, water, water vapors, oils and fats and their ability to be easily heat sealed made them a widely used polymer in the food packaging. PVDC copolymers are also produced by other companies under various trade names, for example Ixan[®] and Diofan[®] from Solvay.

Copolymers of Ethylene

In the 1950s ICI continued to experiment with a range of polar comonomers such as vinyl acetate, methyl acrylate, and n-butyl acrylate, and released ethylene-vinyl acetate (EVA) copolymers on a limited scale to European markets in the late 1950s. Other manufacturers were also involved in the development of EVA with DuPont filing a US patent in 1956 and introducing its commercial EVA in 1960.

Ethylene-vinyl alcohol (EVOH) copolymers were commercialized in Japan by the Kuraray Company in 1972 and in the US and Europe in the early 1980s. EVOH copolymer is produced by transforming the VA group into VOH in a controlled hydrolysis of EVA copolymer. EVOH copolymers offer not only excellent processability, but also superior barriers to gases, odors, aromas and solvents. It is these characteristics that have allowed plastic containers containing EVOH barrier layers to replace many glass and metal containers for packaging food.

Polyesters

Fiber-forming polyesters have been the subject of extensive investigations ever since the American chemist Wallace Hume Carothers at DuPont began his classical research that led to the development of polyamides. However, while Carothers largely confined his research to aliphatic polyesters, John Whinfield and James Dickson, working for the Calico Printers Association in England, investigated aromatic materials. This led to the discovery in 1940 and subsequent successful exploitation of poly(ethylene terephthalate) (PET) by ICI with DuPont licensed by ICI to manufacture PET in the US Mylar (DuPont), Melinex (ICI), and Celanar (Celanese) were among the first PET films used for food packaging. In the Soviet Union, PET was first manufactured in the laboratories of the Institute of High-Molecular Compounds of the USSR Academy of Sciences in 1949.

PET film's outstanding properties as a food packaging material are its tensile strength, excellent chemical resistance, light weight, elasticity and stability over a wide range of temperatures. Rigid PET is also used to make "ovenable" trays for frozen food and prepared meals, where they are preferable to foil trays because of their ability to be microwaved.

In the 1970s, the benefits of biaxial orientation of PET were extended from sheet film to bottle manufacture. Nathaniel Wyeth and Ronald Roseveare were issued a series of patents (filed in 1970 and assigned to DuPont) in 1973 (US patents 3,733,309 and 3,778,214) for a stretch blow molded, biaxially oriented bottle prepared from PET. DuPont chose not to embark on bottle production itself but instead chose to license the product to others. The first PET bottle test market was held in New York State during 1975/76 and the first plastic PET bottles for soft drinks were launched by Pepsi-Cola in 1977, followed soon after by Coca-Cola and other beverage producers. It has been described as probably the biggest single development in the soft drinks industry since the

introduction of the ring-pull can a decade earlier (Turtle, 1984). As a result, important new markets for plastic bottles developed, particularly for carbonated beverages, eventually displacing glass bottles in almost all markets.

Today PET bottles are made by a two-step procedure: an amorphous preform is made first by injection molding and then subsequently stretch-blow-molded to form a biaxially-oriented, semi-crystalline but transparent bottle. Modern PET bottle resins are usually copolyesters, with the most common comonomer being isophthalic acid.

The Society of Plastics Engineers honored Wyeth for Outstanding Achievement in Engineering/Technology in 1981, and in 1986 awarded him its International Award. He was also inducted into the Plastics Hall of Fame in 1986.

In the late 1980s, the high barrier polyester poly(ethylene naphthalate) (PEN) was developed. Although similar to PET, it is more rigid and has improved barrier and mechanical properties. However, the PEN homopolymer is priced at a significant premium to PET (about four times) and therefore, despite its superior properties, it finds little use in food packaging (Rabnawaz et al., 2017).

Polyamides (Nylons)

The early development of the nylons (originally the DuPont brand name for the family of synthetic polyamides), is largely due to the work of Wallace Hume Carothers and his colleagues at DuPont between 1928 and 1937. They first synthesized nylon-6,6 in 1935 after extensive research into condensation polymerization. Commercial production of this polymer for subsequent conversion into fibers was commenced by DuPont in 1939. In 1940, ICI and Courtaulds formed a jointly-owned company in the UK to make and sell nylon 6,6 under license from DuPont.

There is no evidence to support the popular belief that nylon is a contraction of the names of the cities New York and London. In 1940, John W. Eckelberry of DuPont stated that the letters 'nyl' were arbitrary and the 'on' was copied from the names of other fibers such as cotton and rayon. A later publication by DuPont explained that the name was originally intended to be 'No-Run' (run in this context meaning unravel as an early application was for stockings) but was then modified to avoid making such an unjustified claim and to make it sound better. The word nylon was never trademarked.

In an attempt to circumvent the DuPont patents, German chemists investigated a wide range of synthetic fiber-forming polymers in the late 1930s. This work resulted in the successful introduction of nylon-6 (where a six-carbon molecule contained an acid group at one end and an amine group at the other) and between them nylons-6 and -6,6 account for nearly all of the polyamides produced for fiber application. PAs did not become a commercial reality for packaging film applications until the late 1950s. Although considered a specialty film, many presently available food packages would not be possible without PAs. Most PA packaging films in the US are produced from nylon-6 while European films are usually nylon-11, due to lower raw material costs.

In the 1980s, a new polymer, nylon-MXD6, was introduced by the Mitsubishi Gas Chemical Company in Japan. It is made from meta-xylylene diamine (MXDA) and adipic acid and is technically referred to as poly(meta-xylylene adipamide); the 6 indicates the number of carbon atoms in the acid. Nylon-MXD6 has better gas barrier properties than nylon-6 and PET at all humidities, and is more effective than EVOH at 100% RH, due to the existence of the benzene ring in the MXD6 polymer chain (Brown, 1992).

Acrylonitriles

Acrylonitrile (sometimes referred to by its synonym vinyl cyanide, especially by those who seek to raise fears about the safety of the polymer as a food contact material since the monomer is carcinogenic), can be copolymerized with styrene in a ratio of about 70:30 by weight to yield acrylonitrile-styrene-copolymer (ANS). The excellent gas and moisture barriers of these high percentage AN copolymers, coupled with new and improved molding techniques, led to their development for the first carbonated beverage bottles.

Although the nitrile-based plastics could be made into bottles using existing blow-molding equipment, PET could not use this existing technology due to its inclination to crystallize and become hazy at higher temperatures. Thus, early market development work was carried out with nitrile bottles. The first announcement of a commercially available nitrile barrier resin (Barex) for plastic bottles was made by Standard Oil of Ohio (Vistron) in early 1969. This was followed by Monsanto's Lopac[®] (Low Oxygen Permeation Packaging) bottle later that year. Both companies did limited market testing, Barex with Pepsi-Cola and Lopac with Coca-Cola. In 1975 Coca-Cola successfully launched a 950 mL nitrile bottle which Monsanto called Cycle-Safe, but the release in 1977 of toxicological data showing that AN monomer could be carcinogenic at high dosage led to the FDA banning the use of plastic soft drink bottles made with acrylonitrile (Turtle, 1984). The FDA amended its position in 1984 to limit the residual AN content of the finished container to 0.1 ppm. This limit can be met with modern processing methods. However, by this time PET had been successfully commercialized for carbonated beverages, gaining a commanding lead that proved impossible to overcome (Brown, 1992).

Future Outlook for Plastics

Although the possibility of discovering dramatically new polymers is remote, the plastics industry continues to grow, despite a serious setback to growth due to the oil crisis of the 1970s. Current global annual consumption of plastics is about 380 million tonnes (Geyer et al., 2017). Feedstocks for plastics manufacturing consume about 3% of the total petroleum extracted, and of that about 26% of total plastic production is used for packaging (Ellen MacArthur Foundation, 2016).

As the use of plastics in modern society has increased, so too has the environmental impacts associated with its production and disposal. Of the 8.3 billion tonnes of plastics produced since the 1950s, 5.8 billion tonnes was used only once. Of this single-use

plastic, only 9% has been recycled and another 12% incinerated; the rest (4.6 billion) ended up in landfills or the natural environment (Geyer et al., 2017). About 8 million tonnes of plastic waste ends up in the ocean annually, where it can be ingested by marine animals with fatal consequences. The high visibility of plastic marine debris, highlighted through popular television documentaries, has resulted in a 'war' on single-use plastics, although the fact that all paperboard and metal food cans, and almost all glass bottles, are also single-use is ignored.

With modern society so dependent on plastics, and with the food industry a major user of plastics packaging materials, continued research and development toward new combinations of established plastics materials to perform specific functions in more efficient and cost-effective ways is progressing. In order to become more sustainable, some plastics are now being manufactured from biobased materials (see next section). Meanwhile, many multinational food companies have made public commitments to reduce their use of single-use plastics, but this may have unintended environmental consequences. A recent study found that the environmental impacts of using plastics in consumer goods and packaging are nearly four times less than they would be if plastics were replaced with alternative materials (Trucost, 2016).

Biobased Food Packaging

Biobased packaging materials have been defined (Robertson, 2008) as materials derived from primarily annually renewable sources, thus excluding paper-based materials since trees used for papermaking generally have renewal times of 25–65 years depending on species and country. Edible films and coatings are included in this definition.

With the exception of paper-based products, food packaging materials have traditionally been based on what are considered as nonrenewable materials since the time needed to renew them is quite high. This was not always so, and up until the beginning of the 20th century, packaging materials, together with other industrial products such as inks, dyes, paints, medicines, chemicals, clothing and plastics, were made from biologically-derived resources. During the 20th century, petrochemical-derived chemicals replaced biologically-derived resources for most of these industrial products. Now, since the beginning of the 21st century, increasing attention is being given to sustainability and the replacement of nonrenewable resources (particularly those derived from petroleum) with those from renewable sources, essentially plant-derived products and by-products from their fermentation. Plastics production is energy intensive with resins having an embodied energy of 62–108 MJ kg⁻¹ (inclusive of feedstock energy), much higher than that of paper, wood, glass or metals (except for aluminum) (Hammond and Jones, 2008).

Every year, about 170 billion tonnes (1 billion = 10⁹) of biomass are produced by Nature, made up of 75% carbohydrates, 20% lignin and 5% other natural products such as oils, fats, proteins, terpenes, alkaloids and nucleic acids. Only about 3.5% (6 billion tonnes) are utilized by humans with a third (wood) used for energy, paper, furniture and construction, one-third for cereals and one-third for other products like oil seeds, sugar beets and sugar cane, fruits and vegetables. About 5% is used for other nonfood purposes such as chemicals and clothing (Röper, 2002).

While it could be argued that fossil resources are biobased and renewable, it takes more than a million years for biomass to be converted into oil that is used as feedstocks to produce plastics. Since the rate of consumption is much greater than the rate of replenishment, a mass imbalance is produced in the carbon cycle. In contrast, biobased polymers made from materials such as corn starch can be produced and then converted back into biomass in similar time frames (Kijchavengkul and Auras, 2008).

The term 'bioplastics' is ambiguous and should be avoided: it is sometimes used for plastics that are biobased, and sometimes for plastics that are biodegradable, including those that are made from petrochemical-derived rather than renewable biobased resources. Instead, the term 'biobased plastics' should be used to mean plastics derived from biobased materials (Fig. 20).

Biobased materials may (or may not) be biodegradable because biodegradability depends not on the origin of the raw materials but on their chemical composition. Plastics can be classified into four types with respect to whether or not they are biodegradable, and the source of the feedstock used to make them. These four types are 1) biobased and biodegradable; 2) petrochemical-derived and biodegradable; 3) biobased but not biodegradable; and 4) conventional petrochemical-derived but not biodegradable plastics (Figs. 21 and 22).

Biobased and Biodegradable

Starch can be converted into a thermoplastic material by the use of plasticizers and the combined effect of temperature and shear. Packaging made of thermoplastic starch (TPS) typically consists of 70% starch plus plasticizers (glycerine and polyols), fillers, and polycaprolactone (PCL) or poly(vinyl alcohol) (PVOH) which is petrochemical-derived. TPS packages normally retain the hydrophilic characteristics of starch and readily degrade in home composters. They are suitable for low-moisture products such as confectionery and biscuit trays. However, TPS is not really a viable alternative to most petrochemical-derived plastics although nanoclays can be added to improve properties.

Poly(lactic acid) (PLA) is a linear, aliphatic polyester synthesized from lactic acid monomers. It was first synthesized by the French chemist Theophile-Jules Pelouze in 1845 through the poly-condensation of lactic acid into low molecular weight PLA. Almost a century later, DuPont scientist Wallace Carothers found that the heating of lactide in a vacuum produced PLA. The development of PLA has taken a long time to reach production viability. In the early stages of commercialization, the PLA produced was limited to use in biomedical devices because the cost of synthesis was expensive and it was not mass-produced.

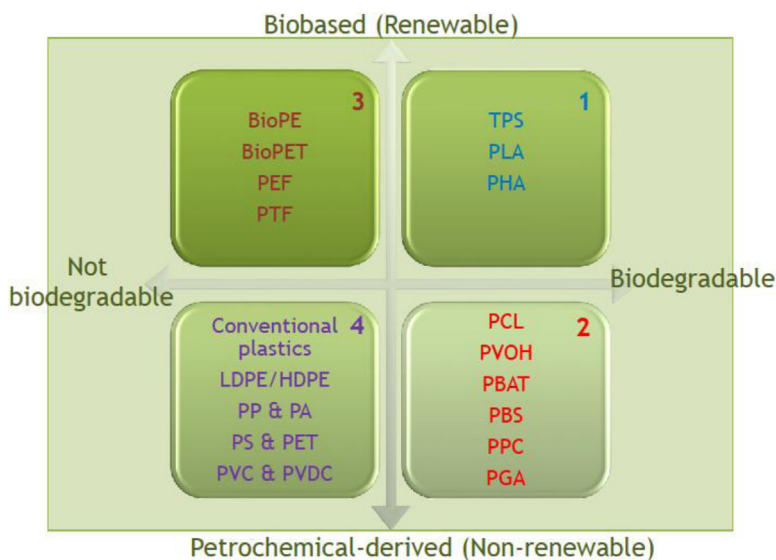


Figure 21 Classification of plastics into four types according to whether or not they are biodegradable and the source of the feedstock used to make them (See text for the meaning of abbreviations).

Cargill has been involved in the research and development of PLA production technology since 1987, and in 1989 Dr. Patrick R. Gruber and coworkers at Cargill invented a low-cost commercial process for producing high molecular weight PLA, receiving US patents 5,258,488, 5,247,058 and 5,247,059 in 1993 assigned to Cargill. The invention related to processes for the continuous production of lactide and lactide polymers from crude lactic acid and esters of lactic acid. In the 1990s, the market for PLA began to expand, with the first pilot plant being set up in 1992 by Cargill, and in 1997 the Cargill and Dow Chemical joint venture founded the company NatureWorks with their preliminary commercial products coming to market under the name Ingeo™ in the US and Biofront® in Japan.

Corbion (formerly known as Purac) has been manufacturing PLA and PLA copolymers for biomedical applications for many years but in recent years has also supplied PLA for food packaging. In 2017 Total and Corbion formed a joint venture Total Corbion PLA to produce and market PLA. In the US, the starting material to produce lactic acid is genetically modified corn, while in Europe, sugar beets are used. In Thailand, sugar cane and tapioca are used.

The major application of PLA in food packaging is as a rigid bottle or tub although it can be used to form a film. The biggest problem is its high water vapor transmission rate. PLA has been certified to be compostable in industrial conditions of 58 °C in the presence of humidity with a processing time of 6 months.

Polyhydroxyalkanoates (PHAs) are microbial polyesters that are produced by nearly 300 bacterial species as intracellular particles that act as energy and carbon reserves. The bacteria *Cupriavidus necator* ferments sugars to a random copolymer of hydroxybutyrate (HB) and hydroxyvalerate (HV). The occurrence of PHA in bacterial cells was first described by Beijerinck in 1888 and the determination of PHA composition was reported by French chemist and bacteriologist Maurice Lemoigne in 1925 in little-read French journals where he referred to the new material as ether-insoluble lipids. From 1923 until 1951, Lemoigne and co-workers published 27 papers, but polymer chemists were not aware that bacteria could produce polyesters before 1960.

The cost of PHAs synthesis is usually a major factor that limits its industrial applications although different carbon sources have been reported to make the production process cost-effective. Beginning in the 1980s, PHAs were produced under the tradenames of Biopol™, Nodax™, Biocycle™, Biomer™, and BioGreen™. Nowadays, the PHAs market is very small. A joint venture Telles, setup by Metabolix (a spin-off from the Massachusetts Institute of Technology founded in 1992 to commercialize technology related to PHAs) and ADM in 2006 was closed in 2012. In 2001 Metabolix had purchased Monsanto's Biopol™ business (originally Zeneca which was formed in June 1993 by the demerger of ICI). Despite the high-performance properties of PHAs including excellent strength and toughness, as well as resistance to heat and hot liquids, their use in food packaging is extremely limited but PHAs producers are optimistic and still see potential for PHAs.

Petrochemical-Derived and Biodegradable

A considerable number of plastics have been available for many years including polycaprolactone (PCL), polyvinyl alcohol (PVOH), poly(butylene adipate-co-terephthalate) (PBAT), poly(butylene succinate) (PBS) and more recently poly(propylene carbonate) (PPC) and polyglycolic acid (PGA). The quantities used for food packaging are very negligible.

Biobased but Not Biodegradable

Bioethylene can be produced by the catalytic dehydration of bioethanol, produced by the fermentation of carbohydrates, followed by normal polymerization to produce polyethylene (PE). It is not biodegradable and has the same properties, processing, and performance as PE made from natural gas or oil feedstocks. The major producers are in Brazil where sugar from cane is used as the starting material. Current applications by multinationals include yogurt cups, fruit juice bottles, and plastic caps and closures for paperboard cartons.

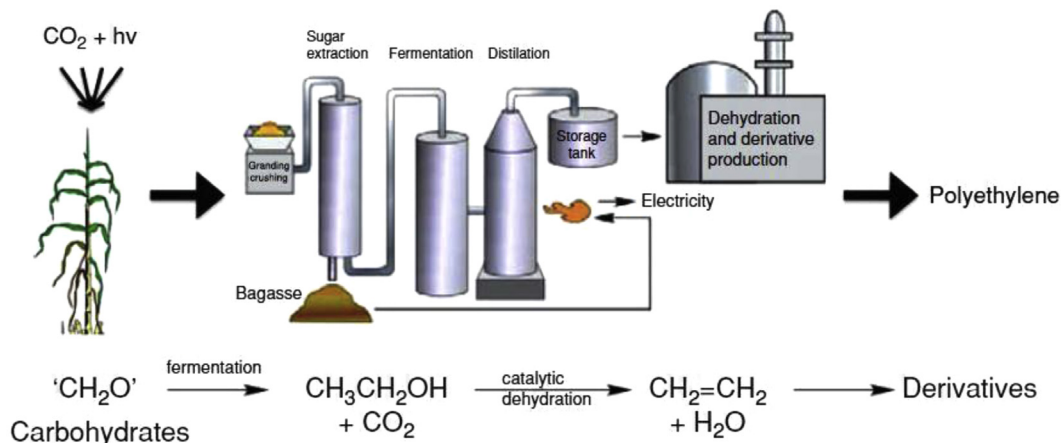


Figure 22 Schematic flow diagram of the production of biopolyethylene from sugarcane via fermentation into ethanol and subsequent dehydration into ethylene. Source: Koopmans, R.J., 2014. With permission from John Wiley & Sons, Ltd., Chichester, England.

In May 2009, The Coca-Cola Co. announced the release of a PET PlantBottle™ made from a blend of petrochemical-derived material [terephthalic acid (TA)] and up to 30% plant-based material (ethylene glycol (EG) from molasses), resulting in a 25% reduction in carbon emissions.

Technology solutions for producing biobased TA have been developed. Virent can produce para-xylene (BioFormPX™) from a wide variety of feedstocks, including sugarcane, corn, and woody biomass and convert this to TA. Gevo, using their Integrated Fermentation Technology® (GIFT®) can convert biomass into isobutanol that can be used to make para-xylene and then TA. Use of the bioTA with bioEG would result in PET that is 100% biobased.

Netherlands-based Avantium was founded in February 2000 as a spin-off from Shell and is an international consortium of industrial companies including Royal Dutch Shell, Eastman Chemical, Akzo Nobel and Pfizer. Avantium's patented technology (YXY) converts biomass into furanics building blocks such as 2,5-furan dicarboxylic acid (FDCA) that can replace TA and be polymerized with EG to polyethylene furanoate (PEF). Production of PEF was given as one example in a 1951 patent titled 'Polyesters from heterocyclic components' by James Gordon Napier Drewitt and James Lincoln (US patent 2,551,731) and assigned to the Celanese Corporation of America.

PEF has superior barrier properties compared to PET with 10 times better O₂ barrier, four times better CO₂ barrier, and twice as good water vapor barrier; it also has more attractive thermal properties with a higher glass transition temperature. In 2016 Avantium formed a joint venture with BASF called Synvina to build a facility in Belgium with the capacity to generate 50,000 metric tons of FDCA per year; in 2019 Avantium bought out BASF. In contrast, Corbion utilizes biocatalytic microbes to consume HMF, resulting in 99% of HMF being converted to high-purity FDCA (Robertson and Sand, 2018). This activity shows much promise. Moreover, Eerhart et al. (2012) reported that production of PEF could reduce nonrenewable energy use by 40%–50% and greenhouse gas emissions by 45%–55% compared to PET on a cradle-to-grave basis. These reductions are higher than for other biobased plastics such as PLA or bioPE.

In 2016 DuPont Industrial Biosciences and Archer Daniels Midland announced a new process for turning fructose into FDME and a pilot plant in Decatur, Illinois, with the capacity to produce 60 tons of FDME a year opened in 2019. DuPont uses FDME to replace dimethyl terephthalate in PET to produce polytrimethylene furandicarboxylate (PTF) through polymerization with bio-PDO (1,3-propanediol). By weight, PTF costs two to four times as much as PET, but compared to PET, PTF is up to 60% stronger and a better gas barrier, which means much less plastic is needed to provide the same level of protection (Robertson and Sand, 2018).

The global production capacity of biobased plastics in 2018 was estimated at 2.11 million metric tons, of which 1.2 million tons were nonbiodegradable and the remaining biodegradable. Biobased plastics remain less than 1% of the total plastics produced.

Sustainability of Biobased Plastics

Are biobased plastics more sustainable than plastics derived from nonrenewable sources? Sustainable polymers were redefined most recently as 'materials derived from renewable feedstocks that are safe in both production and use and that can be recycled or

disposed of in ways that are environmentally innocuous' or 'a class of materials that are derived from renewable feedstocks and exhibit closed-loop life cycles' (Hong and Chen, 2019). However, few disposal methods are innocuous especially in an undefined time parameter; just because they 'can' be disposed of properly is no guarantee that they will be disposed of properly.

In a comprehensive analysis, Weiss et al. (2012) addressed the environmental impacts of biobased materials in a meta-analysis of 44 life cycle analysis (LCA) studies. They found that biobased materials save primary energy and greenhouse gas emissions but may increase eutrophication and stratospheric ozone depletion. Most impacts are caused by the application of fertilizers and pesticides during industrial biomass cultivation. Loss of biodiversity, soil carbon depletion, soil erosion, deforestation, as well as greenhouse gas emissions from indirect land use change, were not quantified in the LCAs. Regardless of definitions and LCAs, biobased plastics will play an increasingly significant role in food packaging in the coming years but are likely to be recyclable rather than degradable (Robertson, 2014).

Aseptic Packaging

Aseptic packaging is the filling of sterile containers with a commercially sterile product under aseptic conditions, and then sealing the containers so that reinfection is prevented; that is, so that they are hermetically sealed. This occurs in a closed system. The first aseptic packaging of food (specifically milk in metal cans) was carried out in Denmark by Niels Jonus Nielsen prior to 1913, and a patent for this process (termed aseptic conservation) was granted in 1921 (British patent 190,810). In 1918, Melville E. Dunkley from Kalamazoo, Michigan received US patent 1,270,798 for a method of sterilizing cans and lids with saturated steam; the cans were then filled with a presterilized product. In 1923, unrefrigerated, aseptically packaged milk from South Africa reached a trade fair in London in perfect condition.

Charles Olin Ball from River Forest, Illinois received US patent 2,029,303 in 1936 (filed in 1930) assigned to The American Can Company (ACC) of New York which used saturated steam under pressure to sterilize the cans and ends. The sterile cans were filled with sterile product and the ends sealed on in a closed chamber which was kept pressurized with steam or a mixture of steam and air. Known as the heat-cool-fill (HCF) system, ACC developed a filling machine in 1933, and in 1938 the HCF process went into commercial use in processing a chocolate-flavored milk beverage. In all three commercial plants were built and operated on this principle until 1945 (Reuter, 1988).

In 1942, at the Avoset plant in Gustine, California, George Grindrod developed the Avoset process based on his 1939 patent (US patent 2,170,196). Whipping cream was sterilized by steam injection and packed in cans, and later in glass bottles. Containers were sterilized in retorts using saturated steam. The retort method of sterilization was eventually abandoned and replaced by a continuous hot-air system, utilizing ultraviolet lamps to protect the filling and closing area. Like the HCF process, the Avoset process is no longer in operation, but it served as a stepping-stone in the evolution of aseptic processing and packaging technology.

In the 1940s, William McKinley Martin from California developed a process in which empty metal cans were sterilized by treatment with superheated steam at temperatures of up to 232 °C for up to 40 s before being filled with cold, sterile product. He received US patent 2,549,216 in 1951 (filed in 1947) assigned to the James Dole Engineering Co. in Nevada.

Martin's aseptic process overcame many of the obstacles that prevented the success of the HCF unit. The use of superheated steam at atmospheric pressure eliminated the need for rotary valves for passing empty cans into the system and finished cans out of the system. Also, the use of atmospheric pressure negated the need for high-pressure construction. This early unit was the forerunner of the Dole Aseptic Canner still in use today. The first commercial units were installed in 1951 for Andersen Pea Soup, and sterilized milk at the Med-O-Milk plant started in 1951 by Ralph Graves and associates in East Stanwood, Washington. Real Fresh Inc. was established in 1952 by Robert Graves and associates at Visalia, California (David et al., 1996). In 1962 Martin patented an improvement for use in aseptic canning systems containing suspended solids such as vegetable soup and beef stew (US patent 3,041,185). Although the Martin-Dole Aseptic Canning System worked well for packaging liquids in metal cans, industry explored possibilities for aseptic packaging in other containers. The first commercial successes with other packages were in Europe, especially through the development by Tetra Pak of machines for packaging milk aseptically in cartons.

At the end of the 1940s, a dairy enterprise (Alpura AG, Bern) and a machinery manufacturer (Sulzer AG, Winterthur) in Switzerland combined their knowledge to develop ultra-high temperature (UHT)-sterilized, aseptically canned milk which was subsequently marketed in Switzerland in 1953. However, this system was not economical, mainly because of the cost of the cans, and Alpura, in collaboration with Tetra Pak of Sweden, began developing an aseptic cartoning system in 1957. As early as the mid-1950s, Tetra Pak had started a technological collaboration with the Swiss industrial group Ursina for the development of long-shelf life milk products. The first Tetra Pak machine for aseptically filling sterilized cartons with sterilized milk was installed in a dairy in Thun, Switzerland, and milk packaged in this manner was first sold in Switzerland in October 1961. The tetrahedral cartons were made with an added layer of thin (9- μm) aluminum to give the required protection, enabling the milk to be kept for up to 6 months without the need for refrigeration (Fig. 23).

The most significant development in the history of the aseptic carton was the commercial release in 1969 of the Tetra Brik Aseptic carton. This packaging system now accounts for more than 80% of the company's packages and dominates the aseptic beverage carton market. In May 1975, the first Combibloc aseptic system was presented to the packaging world, differing from the Tetra Brik Aseptic in being a blank-fed system. Products such as UHT milk and juice became widely available around the world, but not in the US until 1981 when the US Food and Drug Administration (FDA) approved a food additive petition for the use of hydrogen peroxide (H_2O_2) as a sterilant for food contact surfaces. According to the FDA, the final product must not contain greater

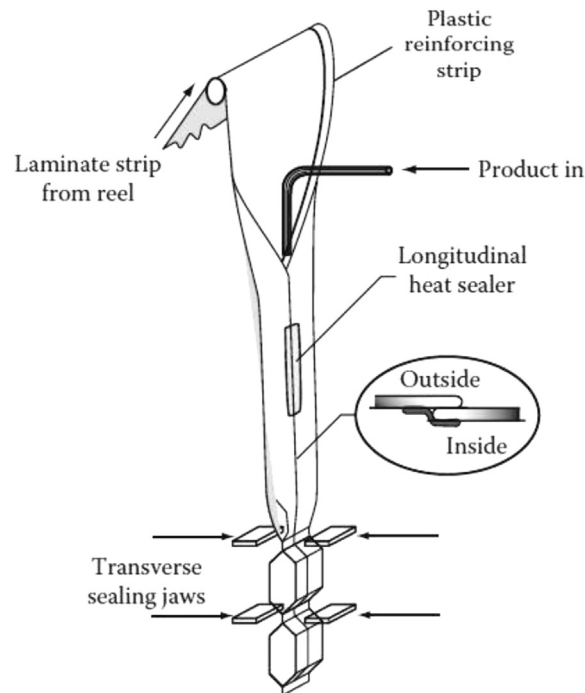


Figure 23 One method of forming cartons from a continuous web; the cross-section of the longitudinal seal is enlarged to show the plastic strip which protects the internal edge of the carton.

than 0.5 ppm H_2O_2 . Their initial approval for the use of H_2O_2 as a sterilant for packaging material that directly contacts food was approved only for polyethylene. The approval was extended to include all polyolefins in March 1984, and in 1985 approval was extended to include polystyrene, modified polystyrene, ionomeric resins, ethylene methyl acrylate copolymer resin, ethylene vinyl acetate copolymer resin and polyethylene terephthalate. In January 1987 approval was extended to include ethylene acrylic acid copolymers (Ansari and Datta, 2003). This provided the impetus for the introduction of various aseptic filling and packaging systems into the US market. Prior to 1981, the Martin-Dole aseptic canning system was the only aseptic filling and packaging system of commercial importance for milk and milk-based low-acid foods.

The Fellows of the US-based Institute of Food Technologists, in connection with the society's 50th anniversary celebrations in 1989, ranked aseptic processing and packaging as "the most significant food science innovation of the past 50 years".

International Paper, the giant forestry and packaging company, recognized the opportunity for a complete carton packaging line and, since 1981 has offered its customers not only the supply of blanks but also form-fill-seal (FFS) machines, following the acquisition of Systempack in Europe in 1981 and the Cherry-Burrell Packaging Division in 1991. They are now being marketed as a web-fed aseptic packaging system and as a blank-fed gable-top system, with packaging materials supplied from International Paper's own manufacturing plants in different parts of the world. More recently, International Paper became the sales agent for the Fuji aseptic packaging system developed by the Japanese company Shikoku, with machines and packages similar to the Tetra Brik Aseptic system (Nermark, 1999).

Despite predictions to the contrary, paper beverage cartons continue to increase in sales worldwide, and they can now be found in more than 170 countries. While the pasteurized milk market in countries such as the US, UK, and Australia has seen a decline in gable-top cartons with a concomitant increase in large-sized HDPE plastic bottles, the aseptic carton market continues to grow, especially in developing countries such as Brazil, Mexico, and China.

Liquid-tight, hermetically-sealed brick-shaped cartons are widely used for the aseptic packaging of a wide range of liquid foods including milk, juices, soups and wines to give packs which will retain the product in a commercially sterile state for years. The end of shelf life (typically 6–9 months) is determined by organoleptic changes as a result of undesirable chemical and physical reactions.

In 2003, two former Tetra Pak China employees joined Tralin Pak, a State-owned enterprise in Shandong, China, and established the company as an alternative supplier for roll-fed aseptic packaging material. It listed on the Hong Kong Stock Exchange in 2010 with a new name, 'Greatview Aseptic' and the following year commissioned a new factory in Halle (Saale), Germany. They now supply aseptic packaging material that can run on Tetra Pak filling machines to over 40 countries.

A wide range of materials is used for aseptic packaging. These include form-fill-seal and prefabricated cartons; tinfoil, ECCS and aluminum cans; glass and plastic (PET, HDPE and PP being the most common) bottles; preformed plastic cups; and sachets and pouches. A detailed list of 27 aseptic packaging systems available in 1985 is presented by Mitchell (1988). Numerous methods are used to sterilize the packaging material with the most commonly used methods including heat, hot water, chemical sterilants (H_2O_2 or peracetic acid), electron beam and radiation or a combination of methods. Most widespread are technologies for sterilization of

packaging materials that use H₂O₂ solutions. The packaging materials are in contact with 15%–35% H₂O₂ solutions during passage through immersion tanks or are sprayed from nozzles with fine droplets of the chemical agent. Alternatively, H₂O₂ may be applied from the vapor phase and then condense on the cold surface of packaging materials in the form of fine droplets. H₂O₂ is removed from the surfaces of the packaging materials by thermal treatments such as hot air or infrared irradiation. H₂O₂ treatment is thus a combination of a chemical and physical procedure.

More recently the aseptic filling of PET bottles has been commercialized by Kronos (Germany) and Sidel (France). Bottles are sterilized at 20 °C with peracetic acid (produced by oxidation of acetic acid by H₂O₂), rinsed with sterile water and filled. A chemically sterilized closure is then applied.

Microwaveable Packaging

The history of the microwave oven began in England in 1940 when two physicists working at Birmingham University (Professors John Turton Randall and Henry Albert Howard Boot) developed an electronic tube (which they named a cavity magnetron) that generated large amounts of microwave energy very efficiently. The unique ability of the magnetron to transmit microwaves at very high power enabled radar equipment to be built that was much smaller, more powerful and more accurate than anything previously designed.

The magnetron was taken to the US in September 1940, and Percy Lebaron Spencer at the Raytheon Manufacturing Company, Newton, Massachusetts received a Defense Department contract to manufacture copies of it for use in radar equipment used by the Allies in World War II. While he was working close to a magnetron, a peanut candy bar melted in his pocket. Although not the first to notice this phenomenon, he was the first to investigate it and this provided the inspiration to use microwaves to heat foods. Spencer then popped some popcorn kernels in front of a waveguide horn, and the concept of using microwaves for heating foods was proven. He filed a patent application for 'Method of treating foodstuffs' in 1945 which was issued in 1950 (US patent 2,495,429). In 1947, he filed another application for 'Prepared food article and method of preparing' that was issued in 1949 (US patent 2,480,679), which showed a pouch specifically designed for microwave heating of an entire cob of popcorn. Both patents were assigned to the Raytheon Manufacturing Company. The first commercial microwave oven was released in 1947 for institutional and restaurant use. When Spencer's basic patent expired in 1967, the microwave oven domestic market grew rapidly, achieving a penetration rate in US households of over 100% (i.e., more than one per household on average) by the early 1990s.

Packaging materials can react in three ways to microwaves: they can reflect the radiation, absorb the radiation or transmit the radiation (so-called RAT characteristics). All the polymers currently used for food packaging, as well as paper products and glass, are transparent to microwaves and do not appreciably react to the microwave field of the oven or significantly modify the power distribution in the oven and are referred to as passive packages. PET-coated paperboard and CPET (crystallized PET) trays are the dual-ovenable packages of choice for ready meals as they can be heated in a conventional oven (up to 190 °C) as well as in a microwave.

Packaging materials that absorb microwave energy and reemit that energy as heat are commonly called susceptors but are also referred to as receptors, absorbers or heater elements; they achieve localized effects such as crisping (surface drying) and browning and are an example of active packaging because they perform functions beyond that of just containment, and enhance the performance of the package. They have been used commercially in various forms since 1975. A broad but not exhaustive listing of US patents concerning packaging for microwavable foods from 1949 to 1999 has been compiled by [Bohrer and Brown \(2001\)](#).

A key microwave susceptor patent was granted in 1986 to Oscar Seiferth (US patent 4,641,005) assigned to James River Corporation, Richmond, Virginia, the patent being a continuation of an application filed in 1979 that was abandoned. The heart of these thin film susceptors were particles of a metal such as aluminum (typically a thickness of 3–6 nm) applied to a heat-resistant surface such as 12 μm biaxially orientated PET film adhesive laminated to a low loss, temperature-stable substrate such as bleached kraft paperboard. These susceptors typically underwent breakup at approximately 200 °C. In many cases, this was inadequate to properly heat the food to achieve the desired crisping and browning ([Fig. 24](#)).

Michael R. Perry and Ronald R. Lentz received US patent 5,571,627 in 1996 assigned to The Pillsbury Company, Minneapolis, Minnesota for a temperature-controlled susceptor structure capable of reaching and maintaining cooking temperatures suitable for crisping and browning foods, but which also had a temperature control mechanism to avoid runaway heating conditions. The susceptor structure consisted of heatset, oriented polycyclohexylene-dimethylene terephthalate (PCDMT) metalized with a thin layer of chromium. However, this patent was never commercialized.

Quilt Wave[®], part of Graphic Packaging International (GPI), Atlanta, Georgia, has been engineered with cells known as 'quilts' that expand when exposed to microwaves. The inflated cells touch the surface of the food and insulate it from the environment to increase the sensible heat flux to the food surface. Channels between the inflated cells allow moisture to evaporate from the food's surface and out of the package, allowing maximum browning and crisping. Quilt Wave[®] consists of a three-layer susceptor rollstock of PET/paper/patterned susceptor-metalized PET. The product can be used either as a stand-alone pouch or package, or as an element in a paperboard carton, tray or sleeve.

Karl Keller from Rafz, Switzerland received US patent 6,607,764 in 2003 for a ventable, microwave-safe food package that contained a valve to release pressure during microwaving. More recently, film structures for bags that permit controlled seal failure when internal steam generated during a microwave heating cycle ruptures the seal have become widely adopted.

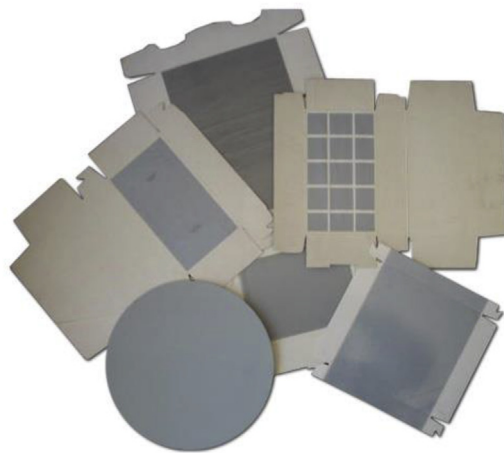


Figure 24 Microwave susceptor package. © February 2011 GAMA Microwave Technology Ltd. mail@gamaconsultants.com.

Smart, Active and Intelligent Packaging

Definitions

The first widely reported use of the term active packaging is generally attributed to the seminal review presented at an EU conference in Iceland in 1987 by Dr. Theodore P. Labuza from the University of Minnesota (Labuza, 1987; Labuza and Breene, 1989). Labuza had just spent a sabbatical year at 3 M working with the Packaging Systems Division on a new time–temperature indicator (TTI) and, during a visit to Tokyo Pack in 1986, had seen many commercial examples of active packaging. He and Curtis Larson from 3 M conceived the term active packaging (short for interactive) for his valedictory presentation to 800 scientists at 3 M at the conclusion of his sabbatical year.

Smart films were first mentioned in the literature in 1986 (Sneller, 1986), the word ‘smart’ being used in connection with selectively permeable films used for MAP. The selective permeability was created by strip lamination of HDPE and PET films, allowing CO₂ to exit the package and preventing excess O₂ from entering. Such films are no longer available.

Smart packages were defined (Wagner, 1989) as “doing more than just offer protection. They interact with the product, and in some cases, actually respond to changes”. The term smart packaging enjoyed a short renaissance in the early 21st century when the Smart Packaging Journal was published online from mid-2002 until 2005. It defined smart packaging as “the use of features of high added value that enhance the functionality of a product, notably mechanical, electronic and chemical features that improve safety and efficiency”. The journal urged readers to forget about all the numerous definitions—active, diagnostic, intelligent, smart, functional and enhancement—to describe smart packaging and accept that it is all one big continuum of functionality. It was suggested that one should think of smart as meaning clever, neat or ‘wow’. Today, smart packaging is used almost exclusively to refer to certain types of intelligent packaging.

Active packaging has been defined as packaging in which subsidiary constituents have been deliberately included in or on either the packaging material or the package headspace to enhance the performance of the package system (Robertson, 2013). The two key words are ‘deliberately’ and ‘enhance’. Implicit in this definition is that performance of the package system includes maintaining (and often improving) the sensory, safety and quality aspects of the food.

Oxygen Absorbers

Oxygen is involved in many deteriorative reactions in packaged foods and therefore methods for removing it from sealed packages have long been the subject of inventions. The earliest example dates from 1869 when Virgil W. Blanchard of Bridport, Vermont received US patent 96,871 for ‘Improvement in preserving fruits, meats, and other substances’ by placing an insert with an alkaline solution of pyrogalllic acid into an air-tight vessel. The acid reacted with oxygen in the headspace and any oxygen that permeated through the rubber seal, effectively acting as an oxygen absorber or scavenger. In 1938 Henrik Tallgren, a Finnish researcher received British patent 496,935 that described the use of iron, zinc or manganese powders to remove O₂ from the headspace of cans. In 1943, Frederick Arthur Isherwood, a researcher at the Low Temperature Research Station at Cambridge University, England received British patent 553,991 that described removing O₂ from a container containing vacuum or gas-packed food in which a metal such as iron absorbed O₂ to form an oxide.

In the US, the removal of O₂ by the catalytic conversion of H₂ to H₂O was first described by King (1955) and applied to spray dried milk powder in initially tinplate cans and later laminate pouches. The package was flushed with a mixture of H₂ (7%) in N₂ and necessitated the use of a palladium catalyst. Ching C. Loo and William P. Jackson were granted US patent 2,825,651 in 1958, assigned to the Carnation Company in Los Angeles, California for an in-package oxygen absorbent obtained by mixing a sulfite and

a metal salt, at least one of which has water of crystallization, followed by compressing the mixture to form pellets. However, it appears that the pellets had a low oxygen-absorbing rate and it was not commercialized.

The use of enzymes and in particular glucose oxidase to remove O_2 has been studied since the initial patent (US 2,765,233) was issued in 1956 to Ben L. Sarett and Don Scott which described the impregnation of a fabric sheet with glucose oxidase and catalase (the latter to destroy the H_2O_2 formed by the former). The concept of incorporating enzymes into a packaging material was overtly described in a 1956 patent issued to Scott (US patent 2,758,932), and in 1958, the first publication on the use of packets or sachets of chemicals in packages to remove O_2 appeared (Scott, 1958), followed 3 years later by another (Scott and Hammer, 1961). The concept was commercialized by Scott's company Fermco Laboratories under the trade name Oxyban.

In 1965 Felix Bioch received US patent 3,169,068, assigned to the US government, for an oxygen absorber comprising sodium bisulfite, an inert carrier having an extended surface, an iron salt, a carbonate and a peroxide. In 1968, Dr-Ing Norbert Buchner received West German Patent 1,267,525 entitled 'Oxygen-absorbing inclusions in food packaging'; it proposed a sodium carbonate powder to absorb O_2 in food packages.

Although almost none of the above-mentioned patents was commercialized, they laid the groundwork for the subsequent development in Japan in 1976 of sachets containing iron powder to absorb O_2 (Harima, 1990). What appears to be the first patent (US 4,113,652) was filed in December 1976 and granted in 1978 to Yoshio Yoshikawa, Akira Ameniya, Toshio Komatsu, Yoshiaki Inoue, and Megumu Yuyama and assigned to Mitsubishi Gas Chemical Company, Inc., Tokyo, Japan for an oxygen absorbent comprising at least one alkaline earth metal sulfite, at least one ferrous compound and free water; it was not commercialized. A later patent (US 4,127,503) filed in July 1977 and granted in 1978 to the same inventors and assignee for an oxygen absorbent comprising a metal powder coated with a definite amount of a metal halide and having a minor amount of water was commercialized under the tradename Ageless[®]; first in Japan and then in the US from 1984. The oxygen scavengers took the form of sachets, cards, labels, and closure linings. The oxygen scavenging activity is triggered by moisture so that the reduced iron is irreversibly oxidized to a stable ferric oxide trihydrate complex (Solovyov, 1999). These systems were soon followed into the commercial market by Mitsubishi's competitor Toppan Printing Company with ascorbic acid-based oxygen scavenger systems and later by other Japanese competitors.

Since then, more than a dozen Japanese companies, two American companies, and a French and Taiwanese company have been actively promoting the use of sachets of readily oxidizable materials as oxygen scavengers for use in flexible and other packages (Brody et al., 2001). More than 400 patents for oxygen scavengers/absorbers were recorded by 2005 (Cruz et al., 2012). Oxygen scavengers are generally regarded as the first widespread commercial application of active packaging.

A more attractive alternative to sachets and pads is the incorporation of O_2 -absorbing materials into the plastics components of packages. The patent literature of the past 90 years contains many ideas for O_2 -absorbing systems that can be incorporated into package structures. Various films with the required reactive ingredients dispersed within the polymer matrix or sandwiched between film layers have been trialed but very few have been successfully commercialized. For example, Yoshiaki Inoue was granted US patent 4,769,175 in 1988 assigned to Mitsubishi Gas Chemical Company, Inc., for a 'Sheet like oxygen scavenging agent'. It was prepared by a process similar to that used in papermaking from a mixture of fibrous material, iron powder, water and electrolytic material. One claim made for this oxygen scavenger was that it could be securely fitted to the inside of a food container or package to prevent it from being eaten by mistake, a fate that meets some oxygen absorber sachets.

In another approach, the UK's Metal Box, (subsequently CarnaudMetalBox (CMB) in 1989 and then acquired by Crown Cork & Seal in 1996) developed oxygen scavenger technology (Oxbar[™]) for use in PET containers in 1988. The active ingredients were nylon-MXD6 and a cobalt salt to catalyze the reaction of oxygen with the aromatic nylon; they were incorporated into the wall of a PET bottle. This system was abandoned by CMB in 1992 for both economic and regulatory reasons, but the technology appears to have been revived by Continental PET Technologies for its multilayer PET beer bottle which was commercialized in 1998 (Brody et al., 2001).

Paul J. Cahill and Stephen Y. Chen received US patent 6,083,585 in 2000 assigned to BP Amoco for 'Oxygen scavenging condensation copolymers for bottles and packaging articles'. It also involved the cobalt-catalyzed oxidation of nylon-MXD6 that was blended with PET and formed the middle layer in a 3-layer PET bottle. Known as Amosorb[™] 2000 oxygen absorber, it was sold to Ciba Specialty Chemicals, Tarrytown, New York in 2000 and marketed as ShelfPlus[™]. In 2009 Albis Plastic GmbH, Mühlenhagen, Hamburg acquired licenses from Ciba Specialty Chemicals to produce and market ShelfPlus[™]. In 2003 ColorMatrix Corp., since 2012 a subsidiary of PolyOne Corporation, agreed to provide global marketing support for Amosorb[™] oxygen scavengers produced by BP Amoco Chemical Co. Amosorb[™] 3000 is a block copolymer of polybutadiene and PET, catalyzed by a transition metal salt, with the PET ensuring compatibilization while the polybutadiene is the oxidizable polymer.

Drew W. Speer, William P. Roberts and Charles R. Morgan received US patent 5,211,875 in 1993 assigned to W. R. Grace & Co. for a material that included a transition metal catalyst and a photosensitizer. The reaction was triggered by light but was designed in such a way as to prevent the rupture of the polymer backbone that might normally occur through oxidation. The material was composed of unsaturated polymers such as poly(1,2-butadiene) which could scavenge oxygen. This product was marketed under the trade name OS 1000 or 2000 by the Cryovac Division of Sealed Air but is no longer available.

Advanced Oxygen Technologies, formerly Aquanautics Corporation, incorporated organometallic ligand compounds analogous to hemes, which bind oxygen, into the plastic liners inside the bottle cap of beverage and particularly beer containers. The oxygen in the headspace of the bottle was removed by the compound, thus prolonging the shelf life of the beer. This technology was commercialized by American bottle-closure producer ZapatA Industries, Inc., Frackville, Pennsylvania and adopted by some breweries in the 1990s but is no longer available.

Antimicrobial Packaging

The burgeoning interest in antimicrobial (AM) food packaging is driven by increasing consumer demand for minimally processed, preservative-free, 'fresh' foods. AM food packaging acts to reduce, inhibit or retard the growth of microorganisms that may be present in the packed food or packaging material itself. Because food spoilage occurs primarily on the surface, incorporation of relatively large quantities of AM agents into the bulk of the food is not justified. A major advantage arising from the use of AM packaging is that only low levels of preservative come into contact with the food, compared to the direct addition of preservatives to the food. However, this was not the case with the early patents in this area.

In 1945 Chester M. Gooding received US patent 2,858,225 assigned to The Best Foods, Inc., New York, for a 'Process of preserving a food product against mold growth thereon comprising wrapping said product in a sheet of material coated with an effective amount up to about 10% by weight of the wrapper' of sorbic acid. Daniel Melnick received US patent 2,724,650 in 1955 also assigned to The Best Foods, Inc., New York for protective packaging materials such as parchment wrappers and waxed cartons for packaging margarine and butter in which fungistatic acids (sorbic or benzoic acid) were incorporated in the wax coating of the outer carton and/or the inner parchment wrapper in an amount not exceeding 2% by weight of the wax coating. Then in 1958 Chester M. Gooding, Daniel Melnick, and Hans W. Vahlteich received US patent 2,858,225 again assigned to The Best Foods, Inc., New York for a 'Method of wrapping and treating wrapped articles, particularly foods, which foster mold growth and which have an irregular external surface or configuration, to render the wrapped articles more resistant to the growth of molds on their outer surfaces' by incorporating sorbic or benzoic acid or their potassium salts into food packaging materials (specifically cellophane, cellulose acetate and glassine). The methods described in the above patents were usefully used in industry despite the fact that the release rate and migration profile of the AMs were not specifically controlled.

The above approaches of using non-volatile AM preservatives such as sorbic and benzoic acid has been extended to propionic acid and its salts, bacteriocins like nisin, natural spices, and silver ions. However, these non-volatile agents require direct contact with the food so that they can exert their AM effect. Packaging systems have been developed that release volatile AMs such as ClO₂, SO₂, CO₂, ethanol and plant extracts (especially essential oils). The advantage of volatile antimicrobials is that they can penetrate the food without the package being in direct contact with the food.

Despite considerable research over the last 70 years to develop and test packaging materials with AM properties to improve food safety and shelf life, few such systems are commercially available. AM films still face limitations and are perhaps best viewed as part of a hurdle strategy to provide safer foods. The legislative status of antimicrobials and their migration into food is also a limiting factor in their commercialization (Yildirim et al., 2018).

Intelligent Packaging

Intelligent packaging has been defined as packaging that contains an external or internal indicator to provide information about the history of the package and/or the quality of the food (Robertson, 2013). The key word in this definition is 'indicator' and includes all the indicators (whether for gases, freshness, temperature or tampering) as well as radio frequency identification (RFID) sensors but not RFID tags or labels because the latter do not indicate the history of the package or the quality of the food but merely its location.

Quality or Freshness Indicators

In this application of intelligent packaging, quality or freshness indicators are used to indicate directly the quality of the product during storage, transport and retailing and in consumers' homes. Intelligent indicators typically undergo a color change that remains permanent and is easy to read and interpret by consumers as well as machines. The indication of microbiological quality is, for example, based on a reaction between the indicator and the metabolites produced during growth of microorganisms in the product.

The general idea of a freshness indicator is not new, with James d'A. Clark from the US Army receiving US patent 2,485,566 in 1949 for a 'Method and device for indicating spoilage'. It was comprised of a transparent cell containing a nutrient medium, non-pathogenic bacteria, and a pH change-responsive indicator. When the temperature rose, the bacteria multiplied and changed the color of the indicator. There are no reports of this indicator being commercialized. In 1962 Ray F. Lawdermit received US patent 3,067,015 for a spoilage indicator for food containers, and more particularly for milk cartons. It involved the direct determination of a volatile metabolite (CO₂) from the microbiologically-spoiling food with a pH dye-based indicator.

Since then a wide variety of freshness indicators reacting to the presence of quality-indicating metabolites has been reported in the scientific literature with most based on a color change of an indicator tag due to the presence of microbial metabolites produced during spoilage. A recent review (Kuswandi, 2017) discusses spoilage, ripeness, leak, and microbial indicators. A few freshness sensors employing RFID are commercially available to monitor the relative humidity, temperature, light exposure, pressure and pH of foods. These tags identify the possible interruptions of the cold chain that are harmful to food safety and quality. However, despite many attempts and several innovative approaches, few quality indicators are in widespread use by the food industry today, due largely to their cost and effectiveness.

Time-Temperature Indicators

Historical Development

Time-Temperature Indicators (TTIs) are devices which integrate the exposure to temperature over time by accumulating the effect of such exposures and exhibiting a change of color (or other physical characteristic). Many devices which can be attached to food

packages to integrate the time and temperature to which the package is exposed have been developed. The first patent for a TTI (US patent 1,927,048) was granted in 1933 to Thomas Midgley and assigned to Frigidaire Corporation of Dayton, Ohio. It was described as a 'Frozen food package comprising a container, a wrapper of transparent material enclosing at least a portion of said container, and a visible character formed of frozen material located between said transparent material and said container, said frozen material being adapted to melt and to permanently change in form when the temperature of the package rises to the temperature below which it is desired to maintain the frozen food. Generically I accomplish these objects by marking the products or the package containing the products in such a way that the original marking is destroyed when the goods have once been thawed or heated above the danger point, and in such a way that the marking cannot be restored even if the goods are refrozen or cooled'.

Since the Midgley patent in 1933, over 300 US and international patents relevant to time-temperature indicators have been issued. During the last 40 years numerous TTI systems have been proposed of which only a few reached the prototype and even fewer the market stage (Taoukis and Tsironi, 2018).

The first commercially available TTI was developed by Honeywell Regulator Company, Minneapolis, MN from a patent assigned to them by James J. Renier in 1963 (US 3,082,624) with the title 'Condition Responsive Devices'. It never found commercial application, possibly because it was costly and relatively bulky. Kwoh H. Hu and Joseph D. Loconti, researchers at the US Army Natick Laboratories, received US patent 3,768,976 for a TTI based on the color change of an oxidizable chemical system controlled by the temperature-dependent permeation of oxygen through a film. The system was contracted to Artech Corp (Falls Church, Virginia) for commercial development (Taoukis, 2010) but achieved limited success.

By 1976 six companies were making TTIs at least at the prototype stage, but by the end of the 1970s very little commercial application of TTIs had been achieved. Research and development activity continued so that by the early 1980s four systems were commercially available. A topical review of the most relevant, recent patents was made by Maschietti (2010), based on the commercial success of the TTIs or their potential commercial viability and the originality of the fundamental principles of the inventions. Although the majority of these devices were developed specifically for frozen foods, there is now widespread interest in TTIs for most categories of food, especially high value foods where the rate of quality deterioration is very temperature sensitive.

Diffusion-Based Indicators

In 1976 Wendell J. Manske received US patent 3,954,011 assigned to 3 M Co., St Paul, Minnesota for a diffusion-based indicator (a blue-dyed ester diffusing along a wick) sold as MonitorMark™. One of the first significant applications of TTIs was the use of this indicator by the World Health Organization to monitor refrigerated vaccine shipments. In 1997, Robert P. Arens, Russell D. Birkholtz, Dee Lynn Johnson, Theodore P. Labuza, Curtis L. Larson, and David J. Yarusso received US patent 5,667,303 again assigned to 3M for a successor TTI: the MonitorMark™ Temperature Monitor and Freshness Check®, based on diffusion of proprietary polymer materials.

Biological Indicators

Kjell Gunnar Blixt, Sven Ivan Arvid Tornmarck, Rolf Juhlin, Karl Rune Salenstedt and Mandayam Tiru received US patent 4,043,871 assigned to Kommanditbolaget Kockums Chemical AB & Co., Malmo, Sweden in 1977 for an enzymatic substrate adsorbed on a solid carrier with a large specific surface area. In 1981 Halina Agerhem and Hans J. Nilsson received US patent 4,284,719 assigned to Kockums Chemical AB, Malmö, Sweden for an improvement on the earlier patent by replacing the inorganic silica carrier with an organic polymer (PVC) to achieve substrate saturation, even at very low substrate concentrations. This led to the commercialization of the VITSAB TTI (VITSAB A.B Malmo, Sweden). The indicator is based on a color change caused by a pH decrease which is the result of controlled enzymatic hydrolysis of a lipid substrate (Fig. 25).

In 2006 Olivier Louvet, Dominique Thuault and Renaud Vaillant received European patent 1,664,334 assigned to Cryolog S.A., Boulogne, France for a biological TTI. Originally marketed as (eO)®, it is currently on the market as TopCryo®, produced by Clock-°T (Cryolog, Nantes, France). In TopCryo® labels, the growth of patented strains of *Carnobacterium maltaromaticum* induces a pH decline of the label medium leading to a color shift from green to red (Fig. 26).

Polymer-Based Indicators

In 1976 Gordhanbhai N. Patel, Anthony F. Preziosi, and Ray H. Baughman received US patent 3,999,946 assigned to Allied Chemical Corporation, Morris Township, New Jersey for a TTI that involved an acetylenic compound having at least two conjugated acetylene groups per molecule that polymerized through a solid-state reaction resulting in a highly-colored polymer. A later patent (US 4,228,126) was granted in 1980 to Gordhanbhai N. Patel and Kwok C. Yee, also assigned to Allied Chemical Corporation, for improvements to the original concept. These patents lead to the release of the Lifelines Freshness Monitor and Fresh-Check® indicators (Lifelines Inc, Morris Plains, New Jersey). The Freshness Monitor could be measured by scanning with a laser optic wand and stored in a hand-held device supplied by the TTI producer but is no longer available. The Fresh-Check® version is for consumers and consists of an 'active' center whose color is compared to the reference color of a surrounding ring (Fig. 27). It is now offered by Temptime Corp., Morris Plains, New Jersey and is the successor to the Lifelines Fresh-Check® TTI.

Miscellaneous

In a novel approach to TTIs, Dietrich Haarer, Tal Gueta-Neyroud, and Husein Salman received US patent 8,968,662 in 2015 assigned to Freshpoint Quality Assurance Ltd., Neshar, Haifa, Israel (now Evigence Sensors) for a TTI that works by chemically dissolving an aluminum layer at a rate that is temperature dependent. A reactive layer is applied to the aluminum layer at the point of

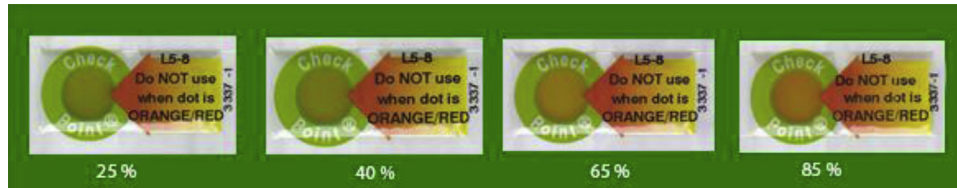


Figure 25 Color changes of a Vitsab L5-8 Smart TTI Seafood Label. <http://vitsab.com/en/tti-label/> accessed on 4 August 2019, with permission.

activation, triggering the chemical process. As the aluminum is etched, the color/visual sign underneath it is revealed. By changing the concentration of the glue or the thickness of the aluminum layer, the label can be adapted to different products with different kinetics (Taoukis and Tsironi, 2018).



Figure 26 Polymer-based Fresh-Check® TTI.

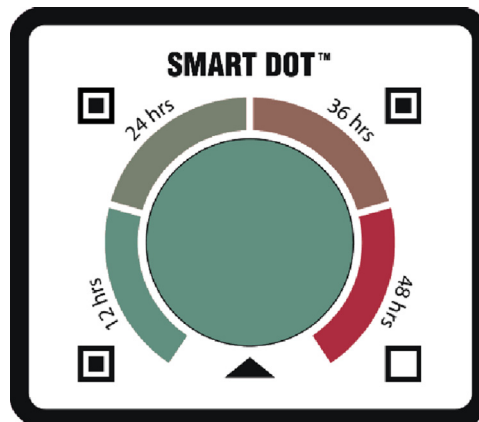


Figure 27 Smart Dot TTI from Evigence Sensors <https://evigence.com/time-temperature-indicators/>.

A novel TTI has been recently developed by FreshStrips B.V., Eindhoven, Netherlands based on a mechanically embossed chiral-nematic polymer network of liquid crystals. A patent (Netherlands 2,019,869) was granted in 2019 to Koen Nickmans and Cornelis Wilhelmus Maria Bastiaansen and assigned to FreshStrips. When exposed to abnormal temperatures, the color of the label changes irreversibly from green to red.

Despite the potential of TTIs to substantially contribute to improving food distribution, reducing food waste, and benefiting the consumer with more meaningful shelf life labeling, their applications have not lived up to initial expectations. More research and development is needed to advance and develop TTI technologies that could help inform stakeholders when foods no longer meet quality or safety-related criteria (Taoukis and Tsironi, 2018).

Intelligent packaging of which TTIs represent the most well-known example has been used commercially since at least 1971 so that historically, intelligent packaging is an antecedent of active packaging.

Gas Concentration Indicators

For many MAP applications (which can include both gas flushing and vacuum), it is helpful to know the gas concentration inside the package headspace and whether or not it is changing over time. Many patents exist for colorimetric O₂ indicators and some have been commercialized, but they suffer from high costs and a lack of reliability due to their reversible nature (Mills et al., 2012).

Modified Atmosphere Packaging

Modified Atmosphere Packaging (MAP) can be defined as the enclosure of food in a package in which the atmosphere inside the package is modified or altered to provide an optimum atmosphere for increasing shelf life and maintaining food quality. Modification of the atmosphere may be achieved either actively or passively. The active modification involves displacing the air with a controlled, desired mixture of gases, a procedure generally referred to as gas flushing. Passive modification occurs as a consequence of the food's respiration and/or the metabolism of microorganisms associated with the food; the package structure normally incorporates a polymeric film, and so the permeation of gases through the film (which varies depending on the nature of the film and the storage temperature) also influences the composition of the atmosphere that develops.

The first recorded scientific investigation into the effect of modified atmospheres on fruit ripening appears to have been conducted by Jacques Étienne Bérard, a professor at the School of Pharmacy at Montpellier in France, who published his findings in 1821. Bérard recognized that harvested fruits utilize O₂ and give off CO₂, and that fruits placed in an atmosphere deprived of O₂ did not ripen as rapidly. He suggested sealing fruits in jars with an oxygen absorber. There is no record of commercial use of this information for nearly 100 years.

However, a remarkable application of the principles of Controlled Atmosphere Storage (CAS) took place in 1865 in Cleveland, Ohio, when Benjamin M. Nyce built a reasonably airtight store that used ice for cooling and a special paste for filtering the atmosphere to remove CO₂. He operated this store for a few years but refused to permit others to use his patented procedures; there is no record of expanded use of his system. In 1858 he received US patent 21,977 entitled 'Improvement in preserving fruits and other perishable substances'.

The first American scientists to investigate CAS were R.W. Thatcher and N.O. Booth of Washington State University. In 1903 they sealed apples in bottles containing a number of different gases. Those in CO₂ held up best and led them to conclude that CO₂ greatly inhibited ripening. The following summer they repeated their experiments with small fruit, after which Booth left the university and the work was discontinued.

In the period between 1907 and 1915, research personnel at the US Department of Agriculture and Cornell University studied the response of several fruits to both lower O₂ and higher CO₂ levels in storage atmospheres. George R. Hill reported in a 1913 Cornell University bulletin that peaches could be prevented from softening by inert gases, especially CO₂. Their work did not result in commercial applications.

The first intensive and systematic research on CAS of fruits was initiated in England in 1918 by Franklin Kidd (later knighted for his efforts) and Cyril West at the Low Temperature Research Station at Cambridge. Various temperatures and atmospheres were used with apples, pears, plums, strawberries, gooseberries and raspberries. The atmospheres were generated passively by fruit respiration and were dependent on the O₂ consumed and the CO₂ evolved by the fruit within a gas-tight building. The first commercial CA store was constructed by a grower near Canterbury in Kent in 1929 and, by 1938, there were over 200 commercial CAS facilities in England.

The knowledge that CO₂ inhibits bacterial growth was not new. In 1877, Louis Pasteur and M. Joubert reported that *Bacillus anthracis* could be killed using CO₂, and 5 years later, the first paper on the preservative effect of CO₂ on extending the shelf life of beef was published in Germany by H. Kolbe. During the period from 1880 to late 1920, about 100 reports were published on the inhibitory effects of CO₂ on microorganisms. In 1930, D.H. Killefer in England demonstrated that lamb, pork and fish remained fresh twice as long in 100% CO₂ at 4 to 7 °C than when stored in air at the same temperatures; E.H. Callow reported similar improvements in keeping pork and bacon. In 1932 R.G. Tomkins and then T. Moran and colleagues reported that mold growth on meat could be retarded with as little as 4% CO₂ in the storage atmosphere. The higher the CO₂ concentration, and the lower the storage temperature, the more effective the inhibition. R.B. Haines reported in 1933 that it took twice as long for some common meat bacteria to multiply in 10% CO₂ at 0 °C than in air at the same temperature. Practical application of these results was made in the shipment of chilled beef carcasses from Australasia to England from the early 1930s, with an atmosphere of 10% CO₂ and a temperature of -1 °C providing a storage life of 40–50 days without spoilage.

F.P. Coyne from the UK reported in 1932 that fillets and whole fish at ice temperature could be kept twice as long if stored in an atmosphere containing a minimum of 25% CO₂ but that undesirable textural and visual changes occurred if the CO₂ concentration exceeded 80%. Although his results were taken to a semi-commercial stage, the technique was never adopted by industry.

A comprehensive study into the use of CO₂-enriched atmospheres for extending the shelf life of poultry meat (chicken portions) was carried out in the US at Iowa State University by *Ogilvy and Ayres (1951)*. The maximum useable CO₂ concentration was 25% because, above this, the meat became discolored; even at 15%, a loss of bloom was sometimes noted.

In the 1950s, Whirlpool Corporation, the US makers of household washers, driers and refrigerators, tried to develop small gas generators for household food preservation of fresh meats and produce using controlled atmospheres together with refrigeration. Their efforts did not prove successful but resulted in the Whirlpool Corporation building larger generators (Tectrol® units) for CA warehouses and, later, truck transports for apples, lettuces and a host of fresh foods. In the 1960s, this technology was spun off to a joint venture company called Transfresh (now Fresh Express and owned by Chiquita Brands International), and it is the world's leading producer of fresh-cut vegetables (*Brody, 2003*).

Recently TransFresh successfully completed a multi-year research and development initiative resulting in a unique Tectrol Storage Solution that utilizes Apio's patented BreatheWay® Technology to deliver a sealed package system with adjustable oxygen transfer rates that react dynamically to changes in temperature and berry respiration for more reliable fresh blueberry storage. Apio is a wholly-owned subsidiary of Landec Corporation.

The first patent for MAP of red meat was issued in 1969 to Douglas Lindley Georgala and Charles Mackenzie Davidson, two workers at Unilever to which British patent 1,199,998 was assigned. It described an atmosphere containing $\geq 70\%$ O₂ and $\geq 10\%$ CO₂, the balance being an inert gas. Under such a modified atmosphere in a gas-impermeable container, beef was still in a fresh condition after 15 days at 4 °C. Preferred gas compositions are 80% O₂ and 20% CO₂ or 75%–85% O₂ and 25%–15% CO₂. Packaging of meat, i.e. chicken pieces and beef steaks and steakslets, plaice fillets and sliced carrots are described in the patent.

In 1931, O. Skovholt and C.H. Bailey showed that storage of bread in atmospheres containing at least 17% CO₂ delayed appearance of mold, with concentrations of 50% doubling the mold-free shelf life. O. Aalund from Norway confirmed these findings in 1961, achieving a mold-free shelf life of 16 days for rye bread packaged in an atmosphere of CO₂. During the 1960s, more extensive research was undertaken in the UK at the Chorleywood Flour, Milling and Baking Research Association into the gas packaging of bakery products using elevated levels of CO₂ to retard mold growth. Unlike flesh foods and fruits and vegetables, baked goods such as bread, pastries and cakes do not benefit from storage at chill temperatures because the rate of staling increases as the temperature is lowered. A large UK bakery used MAP in the late 1960s for cake and achieved shelf life extensions of 4–5 days. However, MAP of baked goods did not become significant until the late 1970s when new labeling regulations in Europe required a listing of all preservatives on the label. Adoption of MAP avoided the need to use, and thus list, preservatives and also gave a longer shelf life. Today, MAP is being increasingly used in the US for preservative-free baked goods with 25% to 55% CO₂ depending on the product.

In the US, vacuum packaging of poultry was introduced by Cryovac[®], followed by the 'boxed beef' concept in 1967, both involving vacuum packaging in low O₂ barrier materials. In these circumstances, the atmosphere around the meat becomes depleted in O₂ (often $< 1\%$ v/v) and enriched in CO₂ ($> 20\%$ v/v), resulting in microbial changes quite different from those observed during aerobic storage. Vacuum-packed boxed beef is then distributed to retail outlets where it is converted into consumer units; vacuum-packed, boxed pork and lamb followed in the 1970s.

A 2002 patent (US 6,342,261) was granted to Kevin C. Spencer and assigned to American Air Liquide, Walnut Creek, California for a method of preserving food using noble gases. It involved the use of a gaseous atmosphere consisting of about 80% to 97% argon and about 3% to 20% of a second gas selected from the group consisting of krypton and xenon. Despite few scientific publications, noble gases were used in a number of food applications including potato chips, processed meats, nuts, beverages, fresh pasta, chilled prepared meals and lettuce with claims of an average 25% improvement in shelf life. Some products, such as fresh pizza, had shelf life improvements of 40% to 50% and nearly 200 different argon-packaged foods could be found on supermarket shelves in the UK and elsewhere in Europe (Spencer, 2005). It is not known if argon is still being used today for the MAP of these and other foods.

In summary, the successful commercialization of MAP in the late 1970s was preceded by over 150 years of scientific research on the inhibitory effects of CO₂ on microbial growth, as well as the effect of gaseous atmospheres on respiring produce. It required the convergence of scientific knowledge, polymeric films, gas flushing and vacuum packaging equipment, and cold distribution chains to achieve the commercial success it enjoys today. Surprising to many is that MAP, in its many manifestations, is now well ahead of the more widely publicized canning, freezing, aseptic packaging, and retort pouch and tray packaging in terms of volume of food preserved (Brody, 2003). Although extension of shelf life is the most apparent advantage of MAP, there are also several other advantages as well as disadvantages.

Conclusion

The historical development of food packaging over the past 200 years began with the introduction of canned foods following the pioneering work of Appert. Then followed the industrialization of processes to make paper and paperboard packages, metal and glass containers not only available on a large scale but also significantly cheaper. The introduction of cellophane, the first transparent flexible packaging material, was hugely influential in the development of self-service retailing of food and was followed over the next 50 years by the commercialization of a wide range of flexible and rigid plastics packaging materials.

The current focus on sustainability has led to renewed interest in biobased food packaging of which there are several very recent and exciting developments. Significant developments related to shelf life and convenience led to the development of aseptic packaging, microwaveable packaging, smart, active and intelligent packaging, and modified atmosphere packaging. But the golden era of food package development, significant as it has been over the past 200 years, is not over. Exciting developments in new materials and processes, as well as variations to existing packages, will continue. Consumers value novelty and so the food packaging industry must continue to innovate or it will stagnate. Material substitution and lightweighting will continue to be central activities in food package development.

The history of packaging is a story of adaption, which provides a clear indication for its future. Packaging will continue to evolve to meet the needs of future markets and value chains. It can be expected to take advantage of future technology and sources of material supply, with an ever-smaller environmental footprint (Twede, 2016).

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