9 Printing Processes, Inks, Adhesives and Labeling of Packaging Materials

9.1 INTRODUCTION

Most packaging materials are printed, so a basic knowledge of the characteristics of the main printing processes is essential. In 594 CE, the Chinese began to practice printing from a negative relief. Their method of rubbing off impressions from a wood block spread along the caravan routes to the western world and, in 1400, the technique of printing with wooden blocks arrived in Europe. The invention of paper, which was to provide the ideal surface for printing, also came from China.

In 1450, Johann Gutenberg invented the printing press in Germany by adapting the wine presses, which had been used in the Rhine Valley since the days of the Roman Empire. He used a recently perfected ink (based on linseed oil and soot) and also invented a functional metal alloy to mold the type. The printed word enabled information and knowledge, which was previously restricted to ecclesiastical establishments, to be widely disseminated and, by 1500, more than 9 million printed books were in circulation.

The basic principle of most printing processes is that ink is deposited on an engraved plate and the inked image transferred to the substrate through contact. This can be performed in several ways when packaging material is to be printed. In direct printing, the inked plate makes direct contact with the packaging substrate. In indirect printing, the engraved plate transfers ink to an intermediate rubber blanket that then transfers the image to the packaging substrate. In stencil printing (e.g., screen printing) the ink is passed through a stencil to the substrate.

There are several different methods of package printing in use today: the conventional printing methods of relief (letterpress, flexography and flexo process), gravure or intaglio, lithography (offset) or planographic and screen or porous and the digital printing methods of ink-jet and electrophotography as shown in Figure 9.1. In the conventional methods, ink is applied to a printing unit such as a cylinder or a plate and is then transferred to the substrate by direct contact.

Plastics such as LDPE, HDPE, PP, PET and EVA copolymer cannot be satisfactorily printed unless their surfaces have been pretreated so as to obtain satisfactory adhesion between the ink and the plastic. This is because their inert, nonpolar surfaces do not permit any chemical or mechanical bonding between them and the ink. Various processes are used, all aimed at oxidizing the surface in some way. These include solvent treatment, chemical treatments, flame treatment and electrical treatment and several of these processes were discussed in Section 5.3.1. In addition to removing dust, oils, greases, processing aids and so on, the surface of the plastic is activated by these processes and becomes more polar.

Photopolymers are light-sensitive plastics used to prepare letterpress, flexographic and offset printing plates. They have been available since 1974 and numerous systems have been developed for producing photopolymer plates. Basically, a photographic process is used in contrast to the photomechanical etching and molding system used to prepare most rubber plates. The photopolymer plate is formed by exposing the photopolymer to UV light through a film negative, which carries the image to be reproduced. Each photopolymer plate is an original derived directly from a negative.

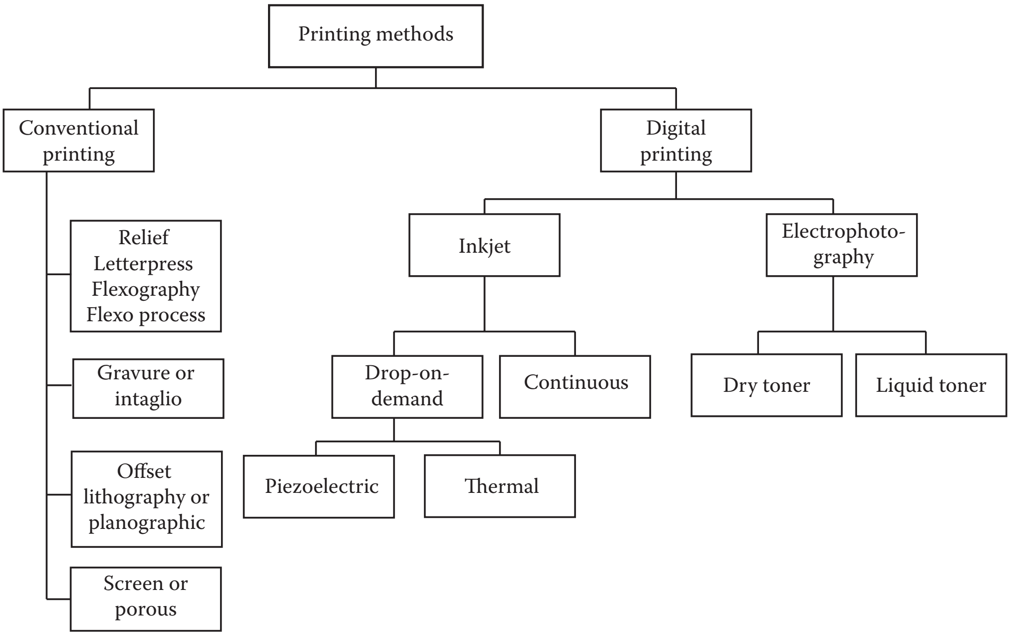

FIGURE 9.1 Classification of printing methods. (Redrawn from Heilmann, J., Digital and conventional packaging printing processes, *Second SustainPack Conference*, Barcelona, Spain, December 4–5, 2006.)

9.2 PRINTING PROCESSES

9.2.1 RELIEF

In this long-established process (commonly known as *letterpress*), the images or printing areas are raised above the nonprinting areas so that the ink rollers touch only the top surface of the raised areas. Originally, metal type was used, in which case the process is called *letterpress*, but this has been largely replaced by synthetic rubber or photopolymer printing plates, in which case the process is called *flexographic*.

9.2.1.1 Letterpress

Letterpress printing presses are of three types: platen, flat-bed cylinder, and rotary, the latter being by far the most common type for printing packaging materials. Plates must obviously be curved for mounting on rotary presses. They receive ink as they contact the inking rollers. An impression cylinder presses the substrate against the inked plate cylinder and transfers the image.

The inks used for letterpress printing are oil-based and slow drying, and have a pasty consistency, which makes the process a difficult one to apply to plastics films unless (like rigid PVC and RCF), they are not too susceptible to the high pressures which often have to be applied. A distinctive feature for recognizing letterpress printing is a “ghost-like” image around each character caused by the ink spreading slightly due to the pressure of the plate on the substrate. A slight embossing or denting sometimes appears on the reverse side of the surface, but the letterpress image is usually sharp and crisp. Letterpress printing is still used for the printing of folding cartons, labels and all types of bags for dry goods.

9.2.1.2 Flexography

Flexography, a relief-printing technique and variation of letterpress printing, is a high-speed method that was developed primarily for printing packaging materials. Introduced into the United States on a fairly broad scale from Germany in the early 1920s, it was known as *aniline* printing because at

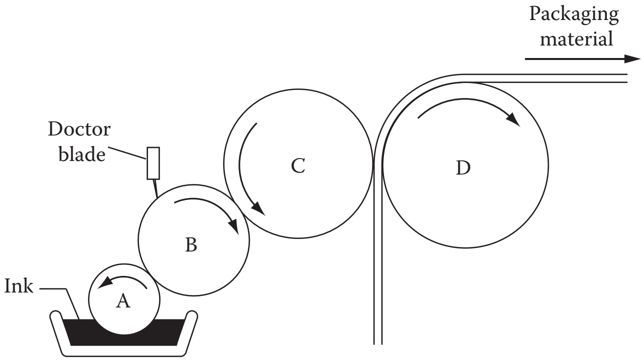

FIGURE 9.2 In flexographic printing, the fountain pan supplies ink to the rubber fountain roller A which supplies ink to the anilox roller B which transfers a uniform layer of ink to the printing cylinder C; the impression cylinder D presses the packaging material against the printing cylinder from which ink is transferred to the packaging material.

that time coal tar dyestuffs (derived from aniline oil) were used as the coloring ingredients for ink. In 1952, the name was changed to flexography. This is defined as a method of direct rotary printing using resilient, raised image printing plates, affixable to plate cylinders of various repeat lengths, inked by a roll or doctor blade wiped metering roll, carrying fluid or paste type inks to virtually any substrate.

Generally, four rollers or cylinders are used. A rubber inking roller (fountain roller) revolves in an ink reservoir and transfers ink to a cavitated metering roller (often called an *anilox roller*) which is engraved such that it can hold ink in its recesses. An optional doctor blade removes excess ink from the surface of the anilox roller so that it transfers a controlled film of ink to the printing plates, which were made of rubber and referred to as *stereos* (an abbreviation for stereotypes), but are now generally made from photopolymer material. The printing plate then transfers this layer of ink to the substrate which is supported by the impression cylinder (Figure 9.2).

Flexographic printing can be carried out with a number of printing stations in sequence: one on top of the other (stack press), with the printing rollers arranged around a central large diameter drum (central impression) or with the printing stations arranged in a straight line (in line). A stack press is used primarily for paper and laminated films, a central impression press for high-quality wide web films and an in-line press for corrugated and folding cartons (Taggi and Walker, 2009). Because the costs of producing the plates are relatively low, flexographic printing is cost effective, especially for short runs.

Thin, fast-drying, solvent-based inks are used in flexography, permitting multicolored printing to be done in one pass provided that oven drying is used. High speeds are possible. A major disadvantage was that very fine half tones were unable to be reproduced, because the inks had a low viscosity and it was difficult to get sharp images, with fine type having a tendency to fill in. However, with the introduction of photopolymer plates, this disadvantage has been overcome.

9.2.1.3 Flexo Process

For flexo process printing, a double-chambered doctor blade delivers the ink to the anilox roller in a closed system that ensures a constant flow of ink. A doctor blade removes excess ink from the anilox roller which is engraved with a very fine screen of 240–320 lines cm^{-1} (600–800 lines in.^{-1}). The engravings distribute a metered amount of ink to the print roller, which has printing plates mounted onto it. An impression roller presses the packaging material against the printing plate and ensures good transfer of ink to the paper (see Figure 9.3).

The quality of reproduction possible with flexo process printing has increased to the extent that it now approaches that of gravure printing. Photographic designs are able to be used.

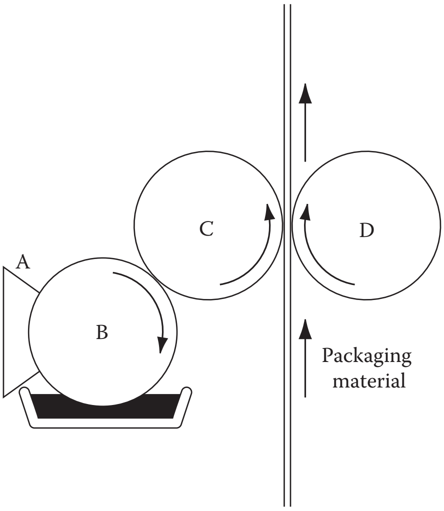

FIGURE 9.3 In flexo process printing, a chambered doctor blade A delivers ink to an anilox roller B which distributes a metered amount of ink to the printing cylinder C; the impression cylinder D presses the packaging material against the printing cylinder.

9.2.2 GRAVURE

Gravure printing was known as *intaglio* from the Italian word for incising or engraving, reflecting the fact that this technique was first practiced in Florence in 1446 by the goldsmith and engraver Finiguerra. Gravure printing (more commonly known as *rotogravure printing* by the packaging industry because cylinders rather than plates are used) consists of a printing cylinder (image carrier), an impression cylinder and an inking system, as shown in Figure 9.4. The printing cylinder (usually made with a chrome-plated copper surface) has the image area etched to form a series of small cells of varying depth so that differing amounts of ink are picked up. During printing, the image carrier is immersed in fluid ink. As the image carrier rotates, ink fills the tiny cells and covers the surface of the cylinder. A doctor blade wipes away excess ink from the nonimage surface of the cylinder. As the cylinder comes into contact with the material to be printed, an impression cylinder (generally covered with a resilient rubber elastomer) presses the material into contact with the tiny cells of the printing cylinder, causing the ink in the cells to be transferred to the material through capillary action.

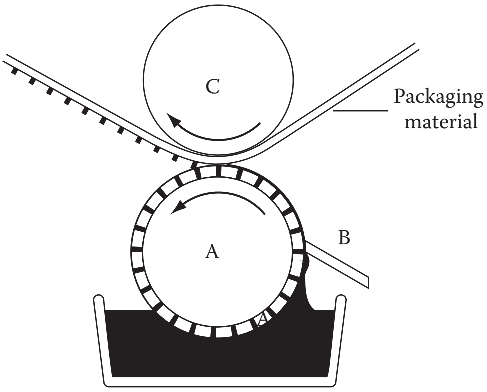

FIGURE 9.4 In rotagravure printing, an engraved cylinder A rotates through the ink, a doctor blade B removes ink from all but the etched recesses and the remaining ink leaves an imprint on the packaging material. C is a rubber impression cylinder.

As with flexographic printing, gravure can print on a wide variety of materials and has found widespread use in the printing of cartons, foils, films and papers for conversion into bags and so on. The ideal substrates are generally smooth in finish (i.e., clay coated, supercalendered papers, films and foils) because effective ink transfer depends on thorough cell contact with the substrate.

Gravure printing can easily be recognized because the entire image area is screened (usually 60 lines cm^{-1} [150 lines in.^{-1}] for normal printing but more if a higher quality is required) to produce the tiny cells in the gravure cylinder. Thus, with a normal screen, there would be 3,600 cells cm^{-2} (22,500 cells in.^{-2}).

The preparation of the printing cylinders is costly and time-consuming and gravure printing is therefore only economical for long production runs. Printing speeds are slower than those obtainable with flexographic printing processes. Despite these disadvantages, gravure printing produces high-quality, multicolor fine-detail printing.

9.2.3 LITHOGRAPHY

Lithographic printing (also known as *offset lithography* and occasionally as *planographic* printing) was invented by the Austrian artist Alois Senefelder in Munich in 1798 as a way to print musical scores more cheaply than by engraving. A lithograph is a print of a drawing done on a stone (usually a limestone). When Senefelder realized his stone-printing method could be used for many other things, he went into business with some partners to operate lithographic presses in the capitals of Europe. For 100 years, lithography was used to print packaging, cards, menus, book illustrations and labels—the first mass forms of advertising. It is still the major form of printmaking today.

Lithography involves printing from a flat surface, the image area being neither raised (as in letterpress and flexography) nor lowered (as in gravure). It is based on the principle that oil and water do not mix.

Oil-based ink is applied evenly through a series of rollers to the *offset* plate cylinder (usually made of aluminum). Water or fountain solution is simultaneously fed via rollers to the plate just before it contacts the inking rollers, as shown in Figure 9.5. Although very little moisture is required, the

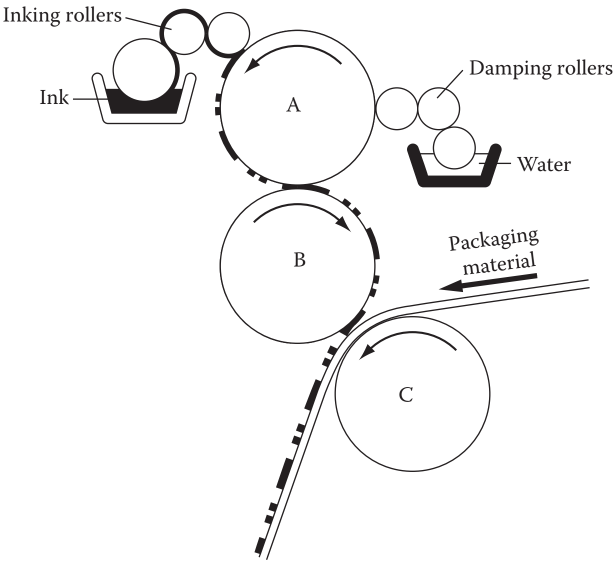

FIGURE 9.5 In offset lithography the image is neither raised nor lowered. It is based on the principle that oil and water do not mix. A is the plate cylinder, B is the offset blanket cylinder and C the impression cylinder.

film of moisture is continuous on the nonimage areas of the plate and acts as a barrier, preventing adhesion of the ink. The plate accepts ink and repels water in the image areas. The image on the plate is transferred or offset to an intermediate or blanket cylinder covered with a rubber blanket. The material to be printed picks up the image as it passes between the blanket and the impression cylinder. The soft rubber blanket creates smooth, sharp images on a wide variety of materials, and is used extensively where illustrations are required on packaging materials.

Offset lithography produces quality printing on both rough and smooth papers, although coated papers are often used as they require less ink and give more brilliance to colors. It is used for printing labels and cartons, and for decorating metal containers, but is rarely used with plastic films. Offset printing plates are cheaper than those for rotogravure and can now deliver almost equivalent print quality.

A process which combines features of both letterpress and lithographic printing methods is known as *letterset* or *dry offset* printing. The term *dry* is used to differentiate it from the standard offset system that uses the incompatibility of water and inks to dampen the surface of the plate or substrate to prevent ink transfer.

In dry offset, ink is transferred by the raised surface of the relief plate to the rubber blanket, which then prints the entire multicolor copy taken from one to as many as six plate cylinders in one operation. No chemical or water action is involved. This method has been especially developed to print round and tapered containers. Letterpress and lithographic inks can be used, with the inks being either heat set or UV cured. However, special letterset inks that provide very low odor printing for food cartons and confectionery wraps that require the use of water-miscible inks are available. Letterset is also used for printing on plastic bottles, cups and tubs and on some metal packages, primarily tubes.

9.2.4 Screen

Screen printing (also referred to as *serigraphy* or *porous* printing) is basically a stenciling process which uses a fine mesh screen made of silk, polyester or metal (fine wire) on which is supported a stencil. The screen is completely coated on both sides with a light-sensitive emulsion, and a positive image of the graphics to be printed is placed on the outside of the emulsion screen. On exposure to intense light, the unshielded emulsion is cured (hardens) after which the shielded, uncured emulsion can be washed away. The nonblocked mesh area of the screen allows ink to pass through the fine mesh.

Ink is forced through the screen onto a substrate by a rubber blade or squeegee. Although screen printing was originally a hand process (and still is in some applications), power-screen presses with mechanical feed and delivery are in common use. Rotary screen presses are also available.

Screen printing inks can be solvent, oil, rubber or water based, but are usually of the drying-oil type and have the consistency of thick paint. Far greater amounts of ink are applied in screen printing compared to other methods of printing, and sometimes the texture of the screen can be recognized on the final image. Extra drying time is frequently needed.

Screen printing is a very versatile printing process, capable of printing on the widest variety of substrates including rounded and irregular surfaces, for example, milk and soft drink bottles. It is ideal for short production runs and is used for imaging glass, box wraps, folding cartons and plastic containers. However, it is relatively low speed and time is required for the ink to dry between colors.

9.2.5 Digital

Digital printing refers to printing from a digital source directly to a variety of substrates using large format and/or high volume laser or ink-jet printers or electrophotography. Digital printing methods do not utilize a physical master (i.e., a fixed printing plate or cylinder) because all the graphic content is in digital form from creation to output. This results in two distinct benefits. First, consecutive copies can be different from each other allowing customization and personalization for selected target groups. Second, the printing process becomes simpler and faster compared to traditional printing methods due to the elimination of master production.

9.2.5.1 Ink-Jet

Ink-jet or impactless printing is a noncontact, pressureless printing process in which tiny drops of ink are projected directly onto a surface for printing without physical contact between the printing device and the substrate. The placement of each drop is controlled electronically. The printing process is termed impactless because no high mechanical impact pressure is involved in transferring ink to the receiving surface as in letterpress printing. Because it is impactless and no platen is required to support the receiving substrate, the process can be used to print on cans, bottles and many other objects. The two main techniques used in ink-jet printers are continuous and drop-on-demand (DoD); DoD is further divided into piezoelectric DoD and thermal DoD. A DoD process uses software that directs the heads to apply between zero and eight droplets of ink per dot, only where needed.

In the continuous ink-jet (CIJ) technique, ink droplets are continually generated by pumping liquid ink to the ink chamber and creating high frequency acoustic pressure waves using a piezoelectric crystal. The wavefield forces ink droplets out from the printhead. The frequency of droplet generation can be 64,000–165,000 droplets s^{-1}. Electrodes apply an electrical charge to the droplets, and the charged droplets are steered using deflectors. Droplets can be either left uncharged or charged selectively according to the signal of the printed image. CIJ technology has been used in applications that require high volume and medium quality, for example, marking and coding of products and packaging.

In the piezoelectric DoD ink-jet technique, the droplets are formed when an electrical signal causes a piezoelectric crystal to expand, which creates a pressure wave forcing a droplet out of the printhead nozzle. The thermal DOD ink-jet, also known as a bubble jet, works in a similar manner, but the pressure wave is generated by heat and vaporizes a small quantity of ink, causing a large pressure increase that propels a droplet of ink onto the substrate. Most production ink-jet printers use piezo printheads.

This printing process has been available since the mid-1960s and has found widespread application for the labeling, coding and dating of packaged food. The tiny droplets of ink are able to be projected into various recesses on the package, which, with the use of inks that adhere to nonabsorbent surfaces, make it ideal for such applications.

9.2.5.2 Electrophotography

Electrophotography, or EP, is the oldest of the nonimpact printing technologies, and was invented by Chester F. Carlson in his Queens, New York, laboratory in 1938. The first of his 28 patents on the subject was issued in 1940 and the first EP copier was sold in 1950. EP printing is often referred to as xerography (from the Greek for "dry writing") or laser printing. Technically, the term "laser" refers to the specific light exposure technology used in the process, but the term laser printer is now generically used to describe any EP printing system (such as an LED printer), regardless of its exposure technology. EP is the printing technique used in copy machines, laser and LED printers, and is the most complex digital printing technology, as well as the most widely used, of the plateless printing technologies.

EP is based on an image carrier surface that is photoconductive and can be charged electrically (Viluksela et al., 2010). Typically, a selenium-coated, photoconductive drum is positively charged. Using a laser or LEDs, a negative of the image is beamed onto the drum, cancelling the charge and leaving a positively charged replica of the original image. Dry or liquid toner attaches to the image areas of the photoconductive surface, and electrostatic forces transfer the toner onto the substrate where it is fixed to the paper. The final stage is fusing, which uses heat and pressure, pressure alone or light to cause the toner binder to melt and permanently adhere to the paper surface.

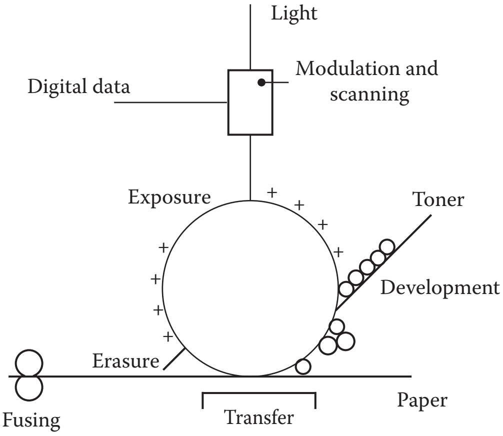

FIGURE 9.6 Principle of digital electrophotography. (Redrawn from Hakola E., Oittinen P. 2009. Principles of digital printing. In: *Print Media–Principles, Processes and Quality*. 2nd edn. Oittinen P., Saarelma H. (Eds). Papermaking Science and Technology, book 13. Paper Engineers' Association/Paperi ja Puu Oy, Helsinki, Finland, pp. 147–172.)

The photoconductive surface is cleaned mechanically and electrically, and charged for the next imaging, as shown in Figure 9.6.

The image quality of digital printing is high enough to be used for packaging. The advantages of digital printing include the possibilities of using variable data, on-demand manufacturing and cost-effectiveness within short print runs. The limitations may include a smaller color gamut compared to traditional presses, format size, productivity and lower printing speed. In addition, the variety of substrates for use is smaller than in traditional printing (Ryynänen et al., 2012).

Lahti et al. (2004) evaluated the printability of three different extrusion coatings used for packaging boards (LDPE, PET and ethylene-*co*-methyl acrylate copolymer) printed using dry toner EP. They showed that adequately high surface energy and surface–charge uniformity were necessary for uniform print quality and toner adhesion. LDPE required surface modification with corona treatment to get good toner adhesion and high print quality, whereas the other two polymer coatings had the required surface energy without corona treatment.

Since the mid-1980s, color EP printing (commonly known as laser printing technology) has been a popular choice by businesses, with high-quality laser printing rivaling more expensive offset color printing for image quality and general appearance. The suitability of digital printing for short runs in the packaging industry has been evaluated and the productivity of a digital packaging line compared with that of a standard packaging line based on an offline offset printing technique (Ryynänen et al., 2012). It was possible to achieve significant cost savings using inline digital printing and converting systems when compared with traditional offline manufacturing systems in short runs. The break-even point was estimated to be in the range of 4000–8000 packages, depending on the package and sheet sizes, with the greatest difference in price per package occurring when the runs were below 2000 packages.

9.3 INKS

9.3.1 INTRODUCTION

The major categories of printing processes are distinguished by whether the ink is held below, on or above, or passes through the surface that contacts the substrate to be printed. Recently, several *no surface* or *contactless* methods have been developed. These different geometries impose different requirements on the inks, which, in turn, largely determine the environmental impacts of each process.

9.3.1.1 Below the Surface

This includes the gravure process, using engraved plates, and the rotogravure process, using engraved cylinders. Ink is retained in depressions in the surface, and is transferred to the substrate when pressed against it. The ink needs to flow readily, and therefore has a relatively high solvent content.

9.3.1.2 On the Surface

This includes the lithographic processes that use differences in surface tension to create areas on the surface that are ink repelling and ink attracting. The type of ink used is invariably one that does not mix with water because the ink-repelling areas are water attracting, and vice versa. A water-based "fountain solution" (often containing some alcohol or equivalent solvent) is used to help keep the ink out of the ink-repelling areas. The ink needs to be somewhat higher in viscosity so that it sits on the surface without spreading. Both the hydrophobic ink solvent (often toluene) and the organics from the fountain solution can add to the environmental impacts. A relatively new process—waterless printing—is a type of lithographic printing that uses mechanical and temperature differences to accomplish the same purpose, with much lower solvent emissions.

9.3.1.3 Above the Surface

This consists of the archetypal printing processes associated with Gutenberg and the linotype machine. Raised letters and lines are inked and the ink is transferred to the substrate. The ink is low viscosity in order to spread uniformly on the ridges, and dries quickly once transferred to the substrate, thus requiring a volatile solvent. There are two major variations, depending on the nature of the plate or roller: letterpress and flexographic, as discussed earlier.

9.3.1.4 Through the Surface

This refers to the screen printing processes, in which the ink is forced through a polyester or wire mesh. A stencil is applied to the top of the mesh, and the ink passes through voids in the stencil, with the mesh regulating the flow of the ink.

9.3.1.5 No Surface

Modern electronics technology has made possible new approaches to transferring ink onto substrates in preset patterns with ink-jet and EP printing, which are now well-established techniques. The requirements for these inks are different and in some ways much more stringent than those for inks for traditional impact printing methods.

9.3.2 INK COMPONENTS

Inks are designed for each of the five main printing processes. Flexography and gravure are known as the *liquid ink* processes, and are based on volatile solvents that evaporate readily at room temperatures. Typically, the evaporative process removes about 35%–40% of the delivered ink volume. Lithography and letterpress are collectively known as the *paste ink* processes, using inks that are essentially nonvolatile at normal temperatures. Screen printing uses inks that fall between these two groups.

Printing inks are mixtures of three main types of ingredients: pigments, vehicles and additives. Pigments used in printing inks include both inorganic pigments (e.g., carbon black and titanium dioxide) and organic pigments, which are frequently dyes rendered insoluble by complexing with a metal ion. Most organic pigments are prepared from azo, anthraquinone and triarylmethane dyes and phthalocyanines. Pigments produce color by selective absorption of light but, because they are solids, they also scatter light. Lead and other toxic pigments have been eliminated from inks for food packaging.

Vehicles generally consist of a resin or polymer with a liquid dispersant, which may be a solvent, oil or monomer. Choice of the vehicle for a printing ink depends on the printing process, how the ink will be dried and the substrate on which the image is to be printed. In lithography and letterpress, where inks are dried by absorption and oxidation, vehicles are generally mixtures of mineral and vegetable oils and resins. Flexographic inks, which are designed to dry quickly by evaporation, can be based on either water or organic solvents such as ethanol, ethyl acetate, *n*-propanol or isopropanol, with a wide variety of resins. Vehicles for gravure inks, which also dry by evaporation, may contain aromatic or aliphatic hydrocarbons and ketones as solvents. Inks for screen printing use organic solvents that are somewhat less volatile than those used for flexography or gravure (e.g., higher glycol ethers and aromatic and aliphatic hydrocarbons). Additives in inks include driers, waxes and plasticizers.

Radiation-curable inks, also known as energy-curable inks, are based on reactive acrylate chemistry where the curing mechanism involves free-radical polymerization. They can be applied by any standard printing process and then cured (polymerized) in line by a brief exposure to either UV or EB (electron beam) energy to form a tough, dry film. They have become the dominant printing technology for food packaging and are used in all of the printing processes to varying degrees. Curing occurs within a fraction of a second, and printing speeds of up to ca. 400 m min^{-1} are possible during continuous printing.

In EB curing, high-energy electrons initiate and complete the curing process. However, because the energy output from a UV lamp is much less, UV-curable inks require *photoinitiators*—chemicals that absorb UV energy and decompose to form free radicals that break the acrylate double bonds to initiate the curing process. UV radiation (ranging from 180 to 400 nm) can be generated by fluorescent lamps and mercury vapor lamps (the latter are more common). The primary wavelengths needed for curing inks are around 250–365 nm.

UV-curable inks consist mainly of acrylic monomers having one to four reactive acrylic groups, although some have higher functionality. They are used as solvents because of their ability to reduce viscosity and combine with other ink components. The inks also contain oligomers such as epoxy, polyester or urethane resins that have been esterified with acrylic acid, and they determine the performance properties of the ink, such as chemical resistance, rub resistance, gloss and coefficient of friction. Significant cross-linking occurs between the monomers and oligomers as both usually contain multiple acrylate groups. The inks also include standard ingredients, including pigments, waxes and defoamers.

There is a second type of UV curing chemistry that employs cationic curing as opposed to free-radical polymerization. Although the inks are also formulated with monomers and oligomers containing reactive double bonds, the photoinitiators decompose on exposure to UV energy to form Lewis acids that initiate the polymerization. The acidic nature of the process somewhat limits the pigments and other ingredients that can be used. Cationic curing is very sensitive to humidity and is also slightly slower than free-radical polymerization. These inks are unsuitable for offset printing for technical reasons but are often used when printing labels (Aurela and Söderhjelm, 2007).

EB achieves a higher degree of cure than UV because the energy input of the EB curing unit is higher. Furthermore, because EB ink film has no residual photoinitiator residues and a lower degree of residual extractables and volatiles compared to UV print, the use of EB is favored over UV for food packaging. The advantages of both EB and UV inks include fast cure speed, room temperature operation, high-quality end products and a decrease in the use of VOCs, incinerators and/or solvent recovery units. A disadvantage is that they are more expensive than conventional inks; as well, the cured ink has a significant volume and so gives a slight relief on the surface. As a result, they are used only where performance advantages outweigh their added cost.

More than 90% of all EB inks and at least half of all UV inks are used for printing packaging materials. While UV and EB inks are mostly used in flexographic printing, new UV offset inks are also being used for UV letterpress applications.

The manufacture of inks consists of dissolving or dispersing resins in organic solvents or oils to produce the vehicle (varnish), mixing and dispersing the pigment or dye into the vehicle and then introducing any additives.

Ink may be deposited on a substrate in various ways in order to obtain the required shade and depth of color. Solid deposition produces a continuous coating of ink, where the shade and depth of color depend on the type and amount of ink deposited on the substrate. Line printing produces a series of lines or crosshatches so that the ink is discontinuous. Shade and depth of color depends on the substrate, ink type, amount of ink and the relative concentration of lines or crosshatching. Dot printing (halftone) consists of a series of ink dots spread over the printed surface. The shade and depth of color depends on the substrate, ink type, amount of ink, dot spacing, dot size and dot density.

An important phenomenon involving inks is "set-off" that can be defined as the unintentional transfer of substances used in printing inks from the external printed surface to the inner, food contact surface. There are three set-off mechanisms: *blocking* (where the ink adheres to the internal surface of the packaging material when stored on reels [printed paper, board or plastics film] or stacked [sheet stock] or nested [articles]), *rubbing* (where the ink layer suffers abrasive transfer when printed stock is stacked or nested, or when a film surface suffers longitudinal friction during the unwinding of a reeled film) and *peeling* (where the ink layer suffers a complete loss of adhesion to the printed substrate and peels away on to the food contact surface). A fourth transfer mechanism (not set-off) can also operate whereby components of the ink migrate by diffusion through the printed substrate to the food contact surface (Bradley et al., 2005).

Recently, migration of printing ink components into food has become a focus of interest following the detection of the photoinitiator isopropylthioxanthone (ITX) in baby milk, milk products and cloudy juices packaged in aseptic cartons in Europe in 2005. More recently the migration of 4-methylbenzophenone and benzophenone (also photoinitiators) from printed cartons into cereals has highlighted the fact that contamination of foods from printing inks is still a problem. This issue is discussed further in Section 22.5.3. The inks used for the major package printing methods are discussed next.

9.3.3 LIQUID INKS

9.3.3.1 Flexographic Ink

9.3.3.1.1 Solvent Based

Typically, alcohols are the solvent of choice with additions of lower esters and small amounts of hydrocarbons to achieve solubility of the vehicle resin and proper drying of the ink film at press speed (Bassemir and Bean, 2009). It is important that all the solvents used are screened to ensure that they do not interact with the printing plates and rolls. Since the 1990s, there has been a trend to phase out solvent-based inks so as to avoid the emission of VOCs, which are implicated in the formation of ground-level ozone and smog.

9.3.3.1.2 Water Based

These have become increasingly common because of environmental concerns about the use of organic solvents in inks. Despite being termed *water-based* inks, the solvent used is not usually 100% water; up to 20% of an alcohol (typically ethanol) is added to increase drying speed, suppress foaming, increase resin compatibility and aid wetting of the plastic substrates. The water-based vehicles are generally emulsions or colloidal dispersions rather than true solutions, and include acrylic emulsion, maleic resin dispersion and styrene-maleic anhydride resins (Bassemir and Bean, 2009).

9.3.3.2 Gravure Ink

9.3.3.2.1 Solvent Based

A wider range of solvents can be used in gravure inks compared with flexographic inks because metal plates are used for gravure printing. Solvents used include aromatic hydrocarbons (toluene being the most common); aliphatic hydrocarbons, alcohols; esters; ketones; chlorinated solvents; and nitroparaffins and glycol ethers, but their use is being phased out.

Technical developments have made it possible to almost completely prevent any toluene emissions in modern rotogravure printing processes. Nonetheless, the question is often asked as to whether ink containing toluene could be replaced by water-based rotogravure ink systems. However, in using water-based inks, there are considerable environmental and qualitative detriments that must be taken into consideration. Ink based on toluene is largely produced using regenerative raw material (resins), whereas water-based ink requires a production process which uses about three times as much energy. In addition, the energy required for drying the ink after the printing process is also higher, which results in increased emissions. In recycling, the color is harder to remove from paper which has been printed with water-based as opposed to solvent-based gravure inks. Finally, the quality of the colors in water-based inks does not meet today's market demands.

Regulations govern the use of toluene in ink, mainly because of the residues of the chemical left in the ink after printing, which could theoretically pose a threat to consumers. Toluene is considered to be a skin irritant, dangerous during long exposure through inhalation and a possible risk to the unborn child. It is also seen as a possible endocrine disrupter which could impair human fertility levels.

9.3.3.2.2 Water Based

These are used for printing paper, paperboard substrates and increasingly for nonpaper substrates as solvent-based inks are phased out. To assist drying of water-based inks, the gravure cylinders are usually engraved or etched with shallower cells so that a thinner ink film is applied. However, to achieve the same relative printing density as solvent-based inks, a greater concentration of pigment must be used.

9.3.3.3 Screen Ink

Relatively little packaging material is screen printed. The two major types of inks used are solvent based and plastisol, although other types including water-based, radiation-cured and two-part catalytic systems are also available (Bassemir and Bean, 2009).

9.3.3.4 Digital Ink

Inks for ink-jet printing must have a low viscosity to enable jetting of droplets, but low viscosity increases dot gain as well as ink spreading and penetration into porous substrates. The inks typically consist of a vehicle (usually 60%–90%), colorant (pigments or dyes; 1%–10%), binder, surfactants, humectants and additives (Hakola and Oittinen, 2009.)

Three types of ink-jet inks are available: (1) water based, (2) oil-nonaqueous-based and (3) hot melt. Water-based inks usually contain >70% water and small amounts of humectants such as glycols to reduce the rate of evaporation and prevent precipitation of dyes when evaporation occurs at the orifice. Biocides are also added to prevent the growth of microorganisms. Oil-nonaqueous-based inks contain more than 50% nonvolatile vehicles such as glycols and fatty acids or their esters. They have low toxicity, minimal corrosive effects and low volatility. Hot-melt inks are solid at room temperature and the printheads are kept at elevated temperature so that the ink is in the liquid state. Molten ink is ejected in discrete drops and rapidly solidifies on reaching the substrate, resulting in very fast drying times. The advantages of hot-melt inks over aqueous inks are their lack of drying at the ink-jet nozzle and excellent image quality on almost any media.

The colorant can be a pigment or dye. Soluble dye inks provide better performance with respect to jettability and nozzle clogging, but the print quality on porous substrates has been limited due to high ink absorption. Pigment-based inks have provided better print quality on porous substrates, because more of the colorant stays on the surface of the substrate. Pigment inks work better with glossy coated papers.

Water-based inks are cheaper than other liquid inks, but have problems with lightfastness and waterfastness. Solvent-based inks have low surface tension, making them well suited to nonporous substrates, and they dry quickly by evaporation. Common solvents include alcohols, ketones and glycols, but as 80%–90% of the ink evaporates, it leads to VOC emissions. Oil-based inks contain hydrocarbons or glycols and dry by absorption; they produce medium print quality. UV-cured inks are becoming popular in label, packaging and wide-format printing, and UV printing is the fastest-growing sector of ink-jet printing (Hakola and Oittinen, 2009).

Most EP printing applications utilize dry toner, that is, toner in powder form. Two-component powder toners are called developers, and consist of larger carrier particles (iron and additives, diameter about 80 µm) and smaller toner particles (pigment and resin binder, diameter 5–20 µm). In the developing station, toner particles attach to the carrier. Application rollers transfer the developer to the photoconductive drum. Toner particles are transferred onto the drum, and the carrier particles return to the developer unit. Additional toner must be added to the developing unit to replace the consumed toner (Viluksela et al., 2010).

9.3.4 PASTE INKS

9.3.4.1 Offset Lithographic Inks

Lithographic ink is basically a concentrated dispersion of pigment in a viscous oil vehicle with various additives. Because the ink comes into contact with water during printing, it must be free from any tendency to bleed or to form an ink-in-water emulsion. The formation of a water-in-ink emulsion is unavoidable, but this does no harm unless the working consistency of the ink is affected.

These inks must resist the chemicals contained in the dampening solution, which is used to keep the plate constantly wetted. A typical ink for metal decoration would consist of organic pigment (15%), acrylate oligomer (40%), acrylate monomer (30%), photoinitiator and sensitizer (8%), tack reducer (4%) and wax (3%), and be dried by simple radiation curing (Bassemir and Bean, 2009). The inks used can also be dried by an oxidative process, which may be accelerated by the use of IR or UV radiation, and, in the case of metal packaging materials, by the use of heat (>150°C) or UV radiation.

9.3.4.2 Letterset Inks

The inks used generally have the viscosity and body of letterpress inks, and are used for the decoration of metal cans and plastic preformed tubs and containers; they are generally dried using heat (metal substrates) or UV radiation.

9.3.4.3 Letterpress Inks

These inks are used primarily for printing corrugated boxes and folding cartons, and drying is essentially oxidative or absorptive. This printing method is being increasingly replaced by water-based flexography (Bassemir and Bean, 2009).

9.3.5 THERMOCHROMIC INKS

Thermochromic inks change color in response to fluctuations in temperature. They are reversible and will change color time after time with the appropriate exposure. These are highly specialized inks that combine standard ink components with one of several color-changing agents described later. Since these inks are used on a wide variety of substrates, they are offered in the typical solvent-based, water-based, plastisol and UV formulations. Depending on the application, thermochromic inks can be applied with a number of printing processes, including offset lithography, flexography, gravure and screen printing.

The two types of thermochromic inks are liquid crystals and leuco (from the Greek word *leukos* meaning white) dyes. Liquid crystal thermochromics are very difficult to work with and require highly specialized printing and handling techniques. For packaging applications, leuco dye thermochromic inks are used in a wide range of applications including product labels. In its cool state, a leucodye exhibits color, and, when warmed, it turns clear or translucent. It takes a 3°C–6°C shift to bring about a change in color.

Alkaline reduction of a dye produces the water soluble alkali metal salt or leuco form, which, on subsequent oxidation, reforms the original insoluble dye. A leucodye is a chemically reduced form of a dye, which, in most cases, is colorless or minimally colored and becomes colored by an oxidation step.

Despite the relatively well-known functionality of thermochromic leucodye-based inks, very little has been published about their colorimetric characteristics. These are significant from an application perspective, and the most important characteristics are the temperature-dependent properties of the complex thermochromic system, the degree of its reversibility and factors that influence this. Kulčar et al. (2010) studied the colorimetric properties of red, blue and black leucodye-based thermochromic inks with an activation temperature of 31°C. The color of the inks was dependent on temperature as well as the thermal history of the sample, which gives rise to color hysteresis. Four characteristic temperatures were ascribed to the two chemical reactions causing color hysteresis. The reversibility of the thermochromic effect diminished approximately linearly with the highest heating temperature.

Some products printed with leucodye thermochromic inks change from one color to another, rather than transitioning from colored to clear. This is achieved by using an ink that combines a leucodye with a permanent-colored ink formulation. For example, a green ink may be formulated by adding a blue leucodye to a yellow ink. In its cool state, the printed ink layer is green and, once warmed, reverts to yellow as the leucodye becomes clear or translucent. Leucodyes can be designed to change color at various temperature ranges, from as low as −25°C up to 66°C. A wide range of colors is also available.

The key components of most thermochromic inks used in packaging are polymer microcapsules 1–10 μm in diameter which is at least 10 times larger than the average pigment particle. The microcapsules provide protection from the components of the ink and contain three interacting chemicals responsible for the overall temperature-dependent color of an ink (Mills, 2009). The first is a leucodye such as fluoran, triphenylmethane lactone or spirolactone. In their ring-closed forms, these dyes are colorless but become highly colored in their ring-opened forms which are generated using a proton donor. The second microcapsule component is a weak acid such as bisphenol A, alkyl *p*-hydroxybenzoate and derivatives of 1,2,3-triazole and 4-hydroxycoumarin that acts as a solvent and proton donor. The third component is a polar cosolvent with a low melting point such as lauryl alcohol or butyl stearate that controls the temperature at which the color change takes place. The dye is usually protonated (i.e., highly colored) when this solvent is a solid, but colorless (i.e., in its leuco form) when it is melted (Mills, 2009). Special considerations are usually involved in printing inks with these relatively large particles because the microencapsulation process cannot completely protect the leucodye system.

Under normal conditions, thermochromic leucodye inks have a shelf life of 6 months or more. After they are printed, they function, or continue to change color, for years. The postprint functionality can, however, be adversely affected by UV light, temperatures in excess of 121°C and aggressive solvents.

As the price of thermochromic inks decreases, their use has become more widespread on food packaging. One obvious area is to indicate to the consumer when the product is at the ideal temperature for consumption and this has been used for beverages such as canned beer and bottled wine. In addition, a thermochromic ink that goes from colored to transparent can hide a warning message that will only be legible once a certain temperature is achieved and this has been used on the lids of disposable coffee cups. Fast-drying, irreversible thermochromic inks have also been formulated for the canning industry. Applied to the end of a can prior to retorting, they can provide a visual verification that the can has been retorted, changing color under the specific conditions of wet heating typical of the retort process. However, they do not indicate that an adequate F_o process has been achieved.

9.4 ADHESIVES

Adhesives are widely used in the packaging industry. The principal uses include the forming and sealing of corrugated cases and folding cartons; the winding of tubes for cores and composite cans; the labeling of bottles, jars and other packages; the lamination of paper to paper, paperboard and foil; and the lamination of plastic films.

Adhesion is the process of bonding two surfaces together, the surfaces being referred to as *adherends*. An adhesive is any substance applied as a thin intermediate layer between two adherends that holds or bonds them together. Adsorption theory states that adhesion results from intimate intermolecular contact between two materials and involves surface forces that develop between the atoms in the two surfaces. The most common surface forces that form at the adhesive-adherend interface are van der Waals forces. In addition, acid–base interactions and hydrogen bonds may also contribute to intrinsic adhesion forces.

Mechanical adhesion is where two porous materials are bonded by adhesive entering the mechanical structure (e.g., paper to paper). Porosity of the adherend will affect the degree of penetration—too little or too much porosity results in a weak bond. Materials such as paper can be coated to control penetration of adhesive or ink.

In contrast, chemical adhesion is the formation of chemical bonds between an adherent and the adhesive. Many adhesives are strongly polar (e.g., starch, PVA and casein). Paper is a polar adherend, whereas LDPE, PP, glass and metals are nonpolar adherends. Many adhesives work using both mechanisms.

The process of establishing intimate contact between an adhesive and adherend is known as *wetting*. To be effective, the adhesive must wet the surface of the adherend. For effective wetting, the surface must be clean and the surface tension of the solvent in the adhesive should be such that the adhesive will wet the surface. Wetting agents are sometimes added to improve this aspect. Polarity will also affect wetting with polar liquids wetting polar surfaces and vice versa. A continuous adhesive film across the surface improves adhesion, which is related to the surface tension and viscosity of the adhesive.

Tack is the ability to form a bond of measurable strength immediately. The elusive nature of the word (and of the concept) stems from the fact that tack results from a composite of several physical observations, parameters and concepts. Tack is the property of an adhesive that allows it to adhere to another surface on immediate contact. It is the “stickiness” of the adhesive while in a fluid or semifluid state.

Tack is not a true physical property of an adhesive, but rather a composite property that has a broad and somewhat qualitative meaning that is very useful in practice. Although there are many different ways to measure tack depending on the application, tack is simply the resistance to separation. Separation is rate and temperature sensitive and involves viscoelastic deformation of the bulk adhesive. The appropriate measurement is the work expended in separation rather than the force used.

Water-borne adhesives are the oldest and still the largest volume class of adhesive used in packaging (Kaye, 2009). Water-borne adhesives are slower drying than solvent-based adhesives, requiring about three times more heat to dry; they also need more time to achieve steady-state performance during production runs. Water-borne adhesives generally do not provide the shear or peel strength that solvent-based systems provide, and, once cured, water-borne adhesives usually do not have the moisture resistance of solvent-borne adhesives. However, water-borne adhesives can withstand wide temperature ranges, are easy and safe to handle and low in cost.

Pressure-sensitive adhesives (PSAs) develop measurable adhesion to a surface simply upon contact or by the application of light pressure. No chemical reaction generally takes place between the substrate and the adhesive, no curing of the adhesive is necessary and no solvent is lost during the adhesion process. Intimate contact between the substrate and the adhesive must be established rapidly and under slight pressure, and the energy necessary to separate the adhesive from the substrate must be sufficient for the specific application. Such a combination of properties is uniquely found in polymers above their T_g, and a balance between compliance and fracture energy is the key when tailoring the properties to a specific application (Creton, 1997).

9.4.1 NATURAL MATERIALS

Until the 1940s, only naturally derived materials were used as packaging adhesives. However, they have now been replaced by synthetic adhesives in many applications.

9.4.1.1 Starch

Starches in the form of amylose and amylopectin are obtained from plants such as wheat, potatoes and maize, and are then subjected to acid hydrolysis to produce smaller chain segments including dextrins. Plasticizers are often added, together with fillers such as kaolin clay and calcium carbonate, which modify the viscosity and reduce cost. Borax can act as a viscosity modifier, increasing tack and preventing microbial growth.

The single largest use of starch adhesives is in the manufacture of corrugated board for shipping containers. Modified starches and dextrins are used in the sealing of cartons, winding of spiral tubes, seaming and forming of bags and attaching labels to metal cans. For the labeling of glass bottles, an alkaline-treated starch adhesive with a special tacky, cohesive consistency is used.

Starch-based adhesives are easy to handle and inexpensive, but suffer from a relatively slow rate of bond formation, poor water resistance and limited adhesion to coatings and plastics.

9.4.1.2 Protein

Natural adhesives based on animal protein were once widely used, but are now used only in specific narrow areas where synthetics have been unable to match their performance. Protein-based adhesives are derived from casein, soybeans or animal hides, bones and connective tissue (collagen).

9.4.1.2.1 Casein

This is produced by the acidification of skim milk which results in the precipitation of the milk protein casein. It has high bond strength and good water resistance, and is the preferred adhesive for labeling glass beer bottles because it provides resistance to cold water immersion and can be removed by alkaline washing. It is also used as an ingredient in adhesives used to laminate aluminum foil to paper (Kaye, 2009).

9.4.1.2.2 Animal Glue

This is a water-borne solution derived from collagen extracted from animal skin and bone by alkaline hydrolysis. It has a high level of hot tack and a long, gummy tack range. It is the standard adhesive used in forming rigid setup boxes (Kaye, 2009).

9.4.1.3 Natural Rubber Latex

This is extracted from the rubber tree *Hevea brasiliensis* and finds use in a variety of self-seal applications since it is the only adhesive system that will form bonds only to itself with pressure (Kaye, 2009). This property (used, for example, in self-seal candy wraps) is called *cold seal* because heat is not required to make a bond. Cold seal adhesives are also referred to as self-seal adhesives and cohesives. The uniqueness of cold seal adhesives is that they seal only to themselves. When a substrate coated with a cold seal adhesive comes into contact with another substrate coated with the same cold seal adhesive, the bond results by using simple digital pressure.

Typically, a water-borne emulsion is printed onto a web substrate using an engraved gravure cylinder. In addition to natural rubber latex, the emulsion also contains water, ammonia, surfactants, antioxidants, antifoam agents, biocides and an acrylic component to aid adhesion to the coated surface (Durston, 2006). In the wet state, cold seal has a shelf life of around 6 months, and after printing, a shelf life of at least 6 months is guaranteed.

Unfortunately, natural rubber latex solutions suffer from limited stability on high shear, high-speed production lines as well as allergy, odor and quality variations that can be problematic. Synthetic alternatives usually do not meet the low tackiness requirements, but some acceptable alternatives are available with the required balance of desired properties while eliminating allergy, odor and consistency problems.

9.4.2 SYNTHETIC MATERIALS

9.4.2.1 Water-Borne Adhesives

These are the most broadly used class of adhesives in packaging, and are mainly resin emulsions consisting of PVA emulsions and stable suspensions of PVA particles in water. The use of EVA copolymers or acrylic esters has greatly improved adhesion capabilities (Kaye, 2009). They are used to form, seal or label cartons, tubes, bags and bottles, and can be formulated to adhere to paper, glass and most plastics and metals. Water-borne adhesives can be formulated to be very water insensitive (for immersion resistance) or water sensitive, depending on need.

9.4.2.2 Hot-Melt Adhesives

Hot-melt adhesives are 100% nonvolatile thermoplastic materials that can be melted by heat and then applied as a liquid to an adherend. The bond is formed when the adhesive resolidifies. Because of their extremely rapid rate of bond formation, they can be used successfully on high-speed packing lines. They can be formulated to adhere to almost any surface due to the wide range of polymers and modifiers used. Their major weakness is the rapid falloff in strength at elevated temperatures which is not generally a problem in food packaging applications.

A typical hot-melt sealant is composed of three primary components: polymers (30%–40%); tackifying resin (30%–40%); and petroleum wax (20%–30%) plus antioxidants, fillers, plasticizers and blowing agents to enhance other properties. The tackifying resins control viscosity as well as wetting and adhesion. The function of the wax is to lower viscosity and control set speed. Fillers are added to opacify or modify the adhesive's flow characteristics as well as to reduce cost (Pocius and Campbell, 2009).

The most widely used polymer is EVA copolymer which is normally run at 180°C. However, the availability of very low MW EVA copolymers has resulted in EVA hot melt that can be run as low as 120°C, leading to energy savings and safer running conditions (Kaye, 2009). Other polymers used include PP, PETs, PAs and polyurethanes (the latter used for adhesive lamination of films such as PP).

9.4.2.3 Solvent-Based Adhesives

Organic solvents have been used as adhesive carrier fluids and diluents, as well as for surface preparation and cleanup. Since the 1990s, environmental and workplace safety regulations on solvents have become increasingly stringent, and there has been a trend to replace solvents and solvent-based adhesives to avoid the emission of VOCs that takes place during formulation, application, drying and curing. As a consequence, the use of water-based and hot-melt adhesives has grown. Today, only a small quantity of solvent-based adhesives is used in specialized applications where water-borne or hot-melt systems do not meet the technical requirements.

9.4.2.4 Pressure-Sensitive Adhesives

PSA is one that remains permanently and aggressively tacky in the dry form and has the ability to bond instantaneously to a wide variety of materials solely by the application of light pressure. No water, solvent or heat is needed to activate these materials (Werblow and Noah, 2009). The desired properties are usually obtained by formulating a miscible blend of uncross-linked or partially cross-linked polymer, a tackifying resin, a plasticizer and various stabilizers. The tackifying resin (usually an oligomer that is fully miscible with the polymer) has the function of substantially increasing the tack of the polymer, while the plasticizer is usually added for processing purposes. The polymers used fall into four broad families, each having their own specific advantages: polyacrylates, silicone polymers, polydienes and random copolymers based on natural rubber and styrene-butadiene rubber, and block copolymers of styrene-diene (Creton, 1997).

9.5 LABELING

Labeling is a means of performing the communication function of packaging, informing the consumer about nutritional content, net weight, product use and so on. Labeling acts as a silent salesman through distinctive branding, as well as facilitating identification at check-outs through the Universal Product Code (UPC). While almost all paper-based packaging (and increasingly metal and plastics packaging) is preprinted, many glass, plastic and metal packages still require labeling.

9.5.1 Glued-On Labels

These are the simplest type and consist of sheet material (typically paper), which has been printed and cut to size. They are attached to the package with adhesive, which is applied either at the time of application, or at the time of manufacture, in which case the adhesive is activated with moisture immediately prior to application. This type of label is widely used for large volume items such as beer, soft drinks, wines and canned foods where high-speed application is required.

For returnable glass and plastic bottles, it is important that the wet strength of the paper is sufficient to ensure that the label can be removed in the bottle washer without repulping.

9.5.2 Self-Adhesive (Pressure-Sensitive) Labels

These can be made from paper, plastic or aluminum foil laminated to paper or plastic, and can be produced to adhere to a wide range of materials. They are supplied with an adhesive coated on the unprinted side and mounted on release paper, which is removed immediately before application to expose the adhesive (Werblow and Noah, 2009).

9.5.3 In-Mold Labels

In-mold labeling is a decorating technique used worldwide for blow molded bottles, as well as injection molded and thermoformed containers. It was pioneered in Europe for injection molding in the early 1970s, and in the United States for blow molding later in that decade. Printed labels can be applied to containers and lids during thermoforming, blow molding and injection molding.

The first in-mold labels (IMLs) consisted of paper, clay-coated on both sides. One side had a heat seal adhesive, and the other an inked surface with an overprint coating to provide protection. Today, such paper labels comprise approximately half the IML market. Labels made with a plastic film form the other portion of the market.

A plastic IML is typically made from HDPE/LDPE blended material and is compatible with a host of plastic containers. What differentiates IMLs from conventional glue-on labels is the heat seal coating that is applied to the back side of the IML stock during the manufacturing process.

IMLs made from film offer better heat, moisture and chemical resistance than those labels made from paper. There are also recycling advantages with film labels. However, the greatest advantage with the use of film is a decorative consideration designated the “no-label” look. This means it is possible to prepare an in-mold-labeled container that actually appears to have no label at all since the unprinted areas of the label blend into the container wall.

IML materials must be able to withstand the container manufacturing process. The heat generated during blow molding presents a challenge to most inks because pigments can change. Varnishes also face special challenges in IML use. The combination of heat and flexing as the container is shaped, followed by sudden cooling, can produce an “orange peel” effect (i.e., a deformation of the smooth surface).

During the in-mold labeling process, a label is placed in the open mold and held in place by vacuum ports, electrostatic attraction or other appropriate means. The mold closes and molten plastic resin is extruded into the mold where it conforms to the shape of the object. The hot plastic envelopes the label, making it an integral part of the molded object. The difference between glue-applied labels and IMLs is that glue-applied labels are on the surface of the object while IMLs are in the wall of the object. The high cost of molds has been a barrier to the wider adoption of in-mold labeling (Werblow and Noah, 2009).

9.5.4 SLEEVE LABELS

A wide range of containers can be sleeve labeled including glass bottles, plastic bottles (extrusion blow molded PP and HDPE bottles as well as stretch blow molded PET) and metal cans. There is almost no restriction regarding the shape of the container. Sleeve labels shrink into or stretch around contours, penetrate variable geometries (such as hourglass shapes) and conform to irregular features (grips or slender necks). Preformed, printed sleeves are slipped over the container (normally a glass or plastic bottle) on line, and then either shrunk in a heat tunnel or (provided that the container is of simple shape) the actual label relaxes onto the container itself. A complex container shape will generally require the sleeve to be shrunk to the contours of the container.

Most shrink sleeves are made of oriented plastic films that shrink around a container when heat is applied. They are used as labels, tamper-evident neckbands and safety shields. Most shrink sleeves are made from PVC or PS film that has been uniaxially oriented to give the desired degree of shrink. The inherent property of uniaxially oriented film—to conform to almost any shape when heat is applied—vastly increases the range and variety of container designs which can use shrink sleeves.

Roll-fed stretch sleeves work well with straight sided single-serve bottles, and are often used with PET bottles. Roll-fed labels are relatively easy to apply, and no heat tunnel is needed.

Shrink-sleeve labels can decorate the complete surface of the container, including the closure if necessary, to provide tamper-evident neck and cap seals while offering maximum graphic space. One limitation to the shape of the sleeved container is the amount of possible shrink; a diameter of 100 mm can be shrunk to a maximum of 40–35 mm. Shrink-sleeve material also provides a UV block.

Sleeve manufacture begins with the extrusion of the film material. This can be PVC, OPP, OPS or PET and is typically 50 µm thick. Depending on the material, up to 75% shrinkage can be achieved. Although it does not have a very environmentally friendly image in some countries, PVC offers a high transparency with a high shrink of 65% at a low temperature. In contrast, OPP (which does not suffer from environmental image problems) offers minimal distortion of the decoration but is less transparent, features a low rigidity and can shrink only 50%. OPP also goes through natural shrinkage, and the sleeve can relax after application. OPS has comparable mechanical and thermal properties. However, OPS is more transparent than OPP and has a minimum vertical shrinkage. At 75%, OPS offers the highest shrinkage, but is not very transparent and has low rigidity. PET has good mechanical properties, is highly transparent, has a high tensile strength and offers shrinkage of 70%. However, the raw material is quite expensive and shrinkage is less controllable, making it more difficult to control than PVC. After film extrusion, the material is gravure- or flexo-printed in up to 10 colors. The sleeve is positioned before the containers enter the shrink tunnel. Shrinking is effected with hot air, infrared radiant heat, steam or a combination of these.

Thin PS foams coextruded with a surface layer for printability are used on beverage bottles. A typical construction would be a foamed PS layer of 300 µm with a 20 µm surface layer. The foamed PS reduces the noise level on filling lines, eliminates partitions in secondary containers and protects glass bottles in vending machines. It also insulates the container. Surface-printed, shrinkable foam labels are used for prelabeling glass, plastic and microwavable containers.

9.5.5 HOLOGRAPHIC LABELS

Holographic labels that incorporate a *hologram* are finding increasing application in food packaging for both marketing and security reasons, specifically in the areas of anticounterfeiting (authentication) and brand protection.

Holograms (from the Greek for *whole* and *writing/drawing*) are part of a family of technologies known as diffractive optically variable devices (DOVIDs). They exhibit a variety of complex images and patterns according to the viewing angle (e.g., if they are tilted or rotated), based on the diffraction of light (International Hologram Manufacturers Association, 2011).

The two most common types of hologram are *surface relief* and *volume*. Surface relief holograms are the most familiar and exhibit a characteristic rainbow-colored pattern or image. The diffractive effect depends on the definition of the lines of tiny ridges and grooves in the surface relief pattern. To prevent damage which would diminish the diffractive effect, the hologram is always protected, either by being laid face down on the document or label, or by being coated with a protective lacquer. In addition, most surface relief holograms require a reflective layer (usually aluminum but other metals or metal oxides can also be used) to bounce light back through the pattern to reveal the image. They are mass-produced mechanically by embossing or casting the relief pattern or image into a thermoplastic film or a viscous coating on a film or paper. PET is the most common substrate but OPP, PVC and paper are also used.

Volume, or reflection, holograms have a very different appearance to surface relief holograms and are generally used for authentication. They are mass-produced through optical copying of a master hologram, so they retain more of the optical properties of that master than the mechanical process of surface relief holograms. This allows them to be used for classical holograms which are fully 3D images, and recent developments also allow the use of color in the image (International Hologram Manufacturers Association, 2011).

9.6 CODING

It has been standard practice in almost all food manufacturing and processing establishments to put a “closed” code (so called because only those with knowledge of the coding system can interpret the code) onto the packaged product. Generally, this code indicates the time of processing and packaging, for example, day and year, or shift, day and year, or hour, day and year. For many canned foods, it has long been mandatory to include such information on the end (lid) of the container in an embossed form, together with a code for the product itself to aid identification of unlabeled cans in the factory and assist in product recalls.

Dating of food products has been known to exist in the U.S. dairy industry since 1917, and in the 1930s U.S. consumers expressed a desire for an open dating regulation to indicate the freshness of their foods (Labuza and Szybist, 2001). Since the advent of the consumer movement in the early 1970s, many different types of open dating systems have been proposed as part of the consumer’s “right to know.” An open date on a food product is a legible, easily read date which is displayed on the package with the purpose of informing the consumer about the shelf life of the product.

The EU’s General Food Law (178/2002/EC) entered into force in 2005 and makes traceability compulsory for all food and feed businesses. Under EU law, “traceability” means the ability to track any food, feed, food-producing animal or substance that will be used for consumption, through all stages of production, processing and distribution. Businesses must be able to identify where their products have come from and where they are going, and to rapidly provide this information to the competent authorities on request.

ISO 22005 gives the principles and specifies the basic requirements for the design and implementation of a feed and food traceability system. It can be applied by an organization operating at any step in the feed and food chain.

GS1 is an international not-for-profit association with member organizations in over 100 countries. The GS1 Traceability Standard is a business process standard describing the traceability process independently from the choice of enabling technologies. It defines minimum requirements for companies of all sizes across industry sectors and the corresponding GS1 Standards used within information management tools.

9.6.1 BAR CODES

A *bar code* is defined as a series of parallel bars and spaces arranged according to the encodation rules of a particular specification in order to represent data (Barthel, 2009). Its purpose is to represent information in a form that is machine readable, typically by scanning devices that are programmed to analyze the structure of the bars and spaces and transmit the encoded data in electronic format to a computer. On June 26, 1974, the first barcode used in a commercial application was scanned; it was a 10 pack of Wrigley's Juicy Fruit gum which is now in the Smithsonian Institute.

Although there are more than 200 bar code symbologies, only are few are in common use with the most popular being EAN/UPC symbology. It is a continuous symbology encoding fixed-length numeric digits and several variants exist. These bar codes always carry a number that is a unique identifier of the item on which the bar code is affixed (Barthel, 2009). EAN/UPC symbology is widely used on consumer products including food and has the advantage of omnidirectional scanning capability.

Since 2005, the EAN/UPC symbology has been managed by the global organization GS1. The GS1 System of Standards are built and maintained through the GS1 Global Standards Management Process (GSMP), a worldwide collaborative forum (www.gs1.org). One of the main building blocks of the GS1 system is the Global Trade Item Number (GTIN) used to uniquely identify trade items at any point in the supply chain. Each trade item that is different from another is allocated its own separate GTIN. Consumer units (the smallest unit intended to be sold to the ultimate end user) are assigned a 12-digit number. Trade items above the consumer unit such as intermediate packs, cartons, packs containing multiple consumer units or standard mixtures of consumer units are assigned a 14-digit number. The GTIN-14 Serial Shipping Container Code (SSCC) uniquely identifies shipping containers and provides a method of linking the physical carton or shipping container to information about its contents. The familiar old GS1 BarCode now comes in a new version called GS1 DataBar (formerly known as Reduced Space Symbology) that is smaller than its predecessor but contains more information.

GS1 EPCglobal, a subsidiary of GS1, is leading the development of radio frequency identification (RFID) technology (see in the following text) by defining and supporting implementation of standards that makes RFID operational across geographies, boundaries and sectors. The Electronic Product Code (EPC) is designed as a universal identifier and is a way to uniquely identify a pallet, case or individual product and is the next generation of the standard bar code. Although it uses a numerical system for product identification, its capabilities are much greater. EPCs are not designed exclusively for use with RFID data carriers and can be constructed to be read by optical data carriers such as 1D and 2D bar codes.

The need to encode more information into a smaller space leads to the development in the 1990s of 2D symbologies and there are now over 20 different 2D symbologies available. Some (known as stacked codes of which the most common is PDF417) consist of 3–90 rows, each of which is like a small linear bar code. ISO 15438 details the specification for the PDF417 bar code symbology; the symbology consists of 17 modules each containing 4 bars and spaces; hence the number "417." The user can decide how wide the narrowest vertical bar (X dimension) is, and how tall the rows are (Y dimension). PDF417 is capable of encoding more than 1100 bytes, 1800 text characters or 2710 digits and can be read by linear scanners, laser scanners or 2D scanners. The physical size of 2D codes is scalable without affecting the amount of information. PDF417 format has been taken up by the airlines and travel industry for the printable boarding passes along with various postal services for printable stamps (Figure 9.7).

The other type are known as data matrix codes and consist of black and white "cells" or modules arranged in either a square or rectangular pattern. They use a small area of square modules with a unique perimeter pattern, which helps the barcode scanner determine cell locations and decode the symbol. Characters, numbers, text and actual bytes of data may be encoded, including Unicode characters and photos. ISO 16022 specifies the data matrix bar code symbology. Most camera-based

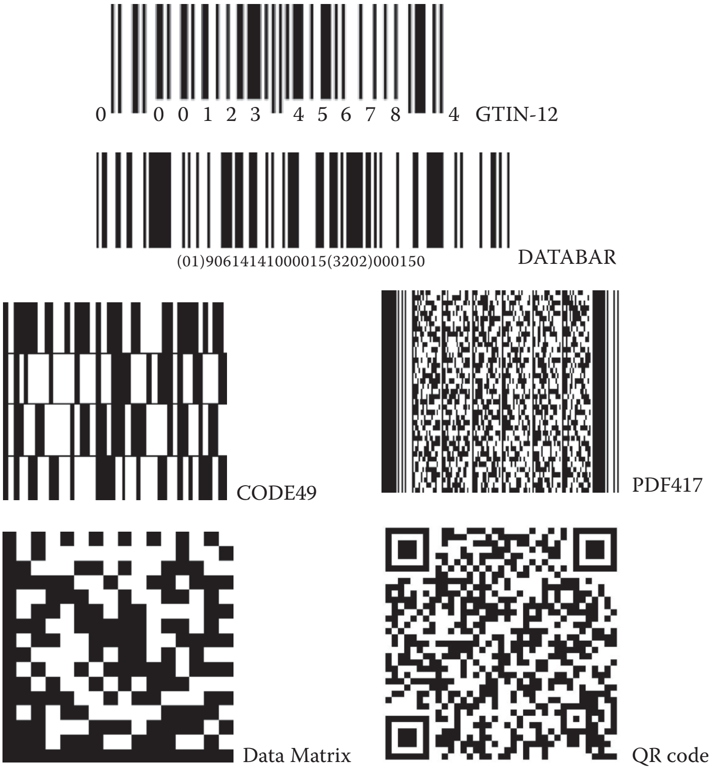

FIGURE 9.7 Examples of various bar code symbologies: GTIN12, DATABAR, CODE49, Data Matrix, PDF417 and QR.

imagers and hand-held scanners have a difficult time reading symbols that contain over 800 characters, although up to 1200 ASCII characters have been successfully encoded and read.

Another type of matrix code is the QR (for Quick Response) code that is machine readable and designed to be read by smartphones; it was invented in Japan in 1994. A QR code contains information in both the vertical and horizontal directions, whereas a bar code contains data in one direction only. As a consequence, QR code holds a considerably greater volume of information than a bar code. ISO 18004 specifies the QR bar code symbology. A company logo can be incorporated into a standard QR code.

Data Matrix from Siemens is a 2D matrix code designed to pack a lot of information (between 1 and 500 characters) on a very small space. The symbol is also scalable but the practical density is limited by the resolution of the printing and reading technology used. Data Matrix is very similar to QR codes and most software can decode both as the differences between them are negligible. The QR code is most popular in Asia whereas Data Matrix is most popular in Europe and the United States.

Several companies offer decoding software for 2D codes that can be installed into many camera phone models, simply by downloading the relevant application. Many of these mobile readers can extend the decoding to enable mobile access and interaction with websites. They are increasingly being used on packages to give consumers access to information, multimedia content, promotional opportunities, retail store locations, discounts, samples and more and can be described as “smart” labels.

A Microsoft Tag or High Capacity Color Barcode (HCCB) is a 2D barcode whose intended use is similar to that of a QR code but can be much smaller because it uses different symbol shapes in geometric patterns and multiple colors or tints to embed more information in less space. A major difference compared to QR codes is that Microsoft Tags do not actually store the information. Instead, the barcode contains a unique ID which the reader application needs to send to Microsoft's servers that then send back all the linked information. In this way, more information or a wider variety of data can be included. The disadvantages are that the reader application needs to be online and there may also be privacy concerns with this server-based approach.

An alternative to 2D codes is SnapTag™ which offers advertisers the opportunity to make their logo a branded mobile interaction point. SnapTags™ are an application-free, branded alternative to a 2D mobile barcode and are created with a brand logo or icon encircled by discrete encoding schemes. Each encoding scheme corresponds to a predetermined response. When photographed with a camera phone and sent to a predetermined phone number or email address, the SnapTag™ is decoded and returns the corresponding data or response to the phone via SMS or MMS message. Microsoft's Tag is capable of including color and can be customized to include a background image, while SnapTag™ uses a brand's identity as the centerpiece of its mobile barcode.

Virtually any printing technology can be used to print bar codes, provided it is precise enough to achieve the necessary quality level to enable accurate scanning. It is preferable that the bar code be printed in black ink on a white background. However, the Microsoft Tags require offset printing due to their small size and the possibility to use color.

9.6.2 RFID

An RFID uses radio frequencies to read information on a small device known as a *tag* or *transponder* with few problems from obstruction or disorientation (Finkenzeller, 2010). Initially, RFID tags were developed to eventually replace barcodes in supply chains. Their advantages are that they can be read wirelessly and without line of sight, contain more information than barcodes and are more robust. To date, RFIDs have been used to increase convenience and efficiency in supply chain management and traceability, being normally applied to secondary or tertiary packaging. However, they still have some drawbacks including cost of implementation, reliability, performance and potential for privacy misuse issues (McCombie and Welt, 2009). If costs can be reduced significantly, then they could find application on individual consumer packages where, in addition to supply chain management, they could also monitor food temperature and ensure food safety if they contained the appropriate sensor (Kumar et al., 2009).

Almost all conventional RFID tags contain a transistor circuit employing a microchip attached to an antenna that is packaged in a way that it can be applied to an object or package. Typically, a tag picks up signals from and sends signals to a reader (also called an interrogator) as depicted in Figure 9.8. The tag contains a unique serial number, but may have other information, such as a customers' account number. Tags come in many forms, such as smart labels that can have a barcode printed on them. The tags can simply be mounted inside a carton or embedded in plastic.

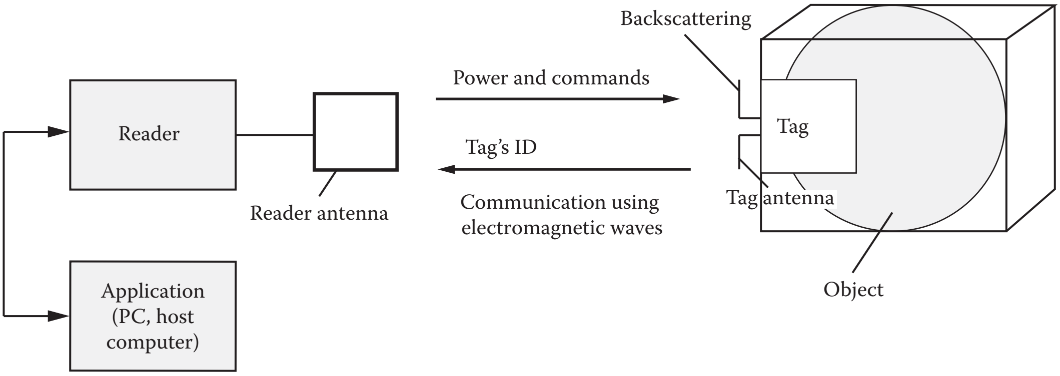

FIGURE 9.8 Key components of a passive UHF RFID system.

The potential in low-cost RFID is split between chip-based technologies and "chipless" tags (also named "RF barcodes"), which can still be interrogated through a brick wall and hold data, but are cheaper and more primitive in electronic performance than chip tags. Chipless RFID tags use material to reflect back a portion of the radio waves beamed at them and are an emerging area of RFID technology for ultra-low-cost RFID applications. However, they are currently confined to the unlicensed RF bands. Although they are less than 1% of the RFID market today, some market projections show that chipless tags will reach 60% of the RFID market before the end of this decade, owing to their low cost and great flexibility. For this reason, chipless RFID is considered the next RFID frontier (Tedjini et al., 2010).

There are three types of RFID tags: active, passive and semipassive. Active tags have an internal power source and are extremely flexible in terms of the functionality they can offer due to their onboard battery, which extends their reading range. Passive tags are not self-powered but are activated by the electromagnetic field emitted by the reader. They are deployed primarily for their low cost and ease of implementation, due to established standards, and find application in the retail supply chain, especially manufacturing, warehousing and distribution (Rida et al., 2010). Semipassive (sometimes referred to as semiactive) tags contain a power source but it is only used to power the circuitry. The radio signal is transmitted using power from the incoming radio signal. These tags are being developed primarily for reusable containers and pallets (McCombie and Welt, 2009). Compared to active or semipassive tags, passive tags have shorter reading distances, require higher power readers and are constrained in their capacity to store data. However, passive tags are simpler in structure, lighter in weight, less expensive, generally more resistant to harsh environmental conditions and offer a virtually unlimited operational lifetime.

An inlay is an RFID microchip attached to an antenna and mounted on a substrate. Inlays are essentially unfinished RFID labels. They are usually sold to label converters who turn them into smart labels. An RFID inlay is a foreign device. Unlike bar codes, which can be incorporated directly into the printed materials of the package and have no inherent volume, RFID inlays have mass, volume and other characteristics that must be considered before being incorporated into a product. Currently, the HF and UHF RFID inlay market is dominated by market segments that are strongly business to business oriented, while the consumer market potential remains almost untapped.

RFID tags fall into four regions in respect to frequency:

1. Low frequency (LF) 30–500 kHz
2. High frequency (HF) 3–30 MHz (typically 13.56 MHz)
3. Ultra high frequency (UHF) 300–950 MHz
4. Microwave (MW) 2.4–2.5 and 5.8 GHz

Each band has its own advantages and disadvantages. LF tags are cheaper than any of the higher frequency tags. Although they are fast enough for most applications, for larger amounts of data, the time a tag has to stay within range of a reader will increase. Another advantage is that LF tags are least affected by the presence of fluids or metal. The disadvantage of such tags is their short reading range (<30 cm). Frequencies for LF and HF tags are license exempt and can be used worldwide; however, frequencies approved for UHF tags differ from country to country and require a permit. The range of RFID tags is typically larger at higher frequencies (>1 m for HF and >3 m for UHF) and, therefore, most pallet-level RFID applications make use of 900 MHz or 2.4 GHz. Furthermore, since the passive components (both inductors and capacitors) are smaller at these higher frequencies, total tag size and thus cost can be reduced.

Research on passive tags, particularly UHF tags, is still very active in order to ensure interoperability, low cost and data security. The interoperability is needed since there are three frequency bands worldwide. Roughly, the operating frequency bands are 865–869 MHz for Europe, 902–928 MHz for the Americas and the United States and 952–954 MHz in most of Asia including Japan and China (Tedjini et al., 2010). Where cargo or containers are imported and exported from different regions of the world using a secure RFID system, an RFID tag is required to have sufficient bandwidth to operate globally, and this imposes very stringent design challenges for the antenna designers. The interoperability requires the development of efficient, miniaturized antenna able to cover all three RFID UHF bands.

Unfortunately, for item-level tracking, these UHF frequencies do not work particularly well, due to the presence of substantial amounts of metal (e.g., food cans) and RF-absorbing fluids (e.g., water, juice and milk). Highly dielectric materials (liquids) and conductors (metal), even in small amounts, can drastically change the properties of a tag antenna, reducing efficiency and shortening the read distance, sometimes to the point of becoming completely unreadable at any distance. Therefore, at this time, it appears that 13.56 MHz or lower is the most attractive frequency, since absorption is substantially reduced at lower frequencies. In general, therefore, the sweet spot for item-level RFID will likely exist at 13.56 MHz, though there is currently a push for developing 900 MHz solutions as well (Subramanian et al., 2005).

Recently, Singh et al. (2011) evaluated an innovative system for improving the readability of passive UHF RFID tags operating between 902.25 and 927.25 MHz in conjunction with reusable PP plastic containers (RPCs) filled to their maximum capacities with either carbonated soda packaged in aluminum cans or water in PET bottles. The system involved the inclusion of an energy transfer device (ETD) consisting of a coaxial transmission line on the bottom of the RPCs that passively transferred RF signals to interior regions of the unitized loads, thereby improving the readability of all RFID tags attached to the RPCs by nearly 97%.

Integrating sensors with RFID tags renders the whole system capable of not only tracking, but also providing real-time cognition of aspects of its status or its environment (e.g., storage conditions of perishable food). The ultimate goal is to create an easily deployable and rugged intelligent network of RFID-enabled sensors.

RFID tags are often a complement, but not a substitute, for UPC/EAN/GTIN barcodes and may not ever completely replace barcodes, due in part to the higher cost of tags and the advantage of multiple data sources on the same object. The new EPC was not designed exclusively for use with RFID data carriers, and, along with several other schemes, is widely available at reasonable cost.

Printed electronics provide a potential pathway toward the realization of ultra-low-cost RFID tags for item-level tracking of consumer goods. Ink-jet printing can be used efficiently to print electronics on paper substrates. In the design and fabrication of antennas for RFID tag devices operating in the UHF and MW range, paper substrate materials and ink-jet printing processes with conductive ink have been used to guarantee mechanical flexibility and ultra-low production costs of the antenna. Inks containing silver nanoparticles are usually selected in the ink-jet printing process to ensure good metal conductivity. After the silver nanoparticle droplet is driven through the nozzle, a sintering process is necessary to remove excess solvent and material impurities from the depositions (Rida et al., 2010).

Recently, researchers have built a 13.56 MHz-operated 1-bit RFID tag that can be printed directly onto cereal boxes and potato chip bags using a gravure printer (Jung et al., 2010). The tag uses a semiconducting ink containing carbon nanotubes that will hold an electrical charge. The current prototypes, estimated to cost 3 cents per unit, are three times the size of a typical barcode, and can only store 1 bit of information which is just enough to give either a yes or no response to an RFID reader. Improving the resolution and accuracy of the printer should allow smaller tags that carry more information. There is also a need to improve the circuit so that it emits higher power signals as at present the reader only works up to 10 cm away which is unacceptable at a checkout line.

Orecchini et al. (2011) reported the development of a new antenna design methodology to minimize the amount of both paper substrate and ink-jet conductive ink to guarantee mechanical flexibility and ultra-low cost mass production of RFID tags. Prototypes made by reducing the antenna size and removing metal material where the surface current density was negligible validated the proposed design methodology.

To qualify as intelligent packaging, RFID tags must contain an indicator that provides information about aspects of the history of the package (e.g., its temperature) or the quality of the food. Intelligent RFID tags with sensors are now being commercialized and are discussed in Section 15.4.1.4.

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