INKS

1. Introduction

According to most historians, writing ink was first prepared and used by the Chinese and the Egyptians as early as 2600 BC. These early inks were probably composed of carbonaceous materials such as lamp black or soot mixed with animal glue or vegetable oil vehicles. Reference is also made to the Chinese invention of solid ink blocks and pellets similar to India ink as it is known today; the Chinese invention had its origin during the period 220–419 AD. Writing-ink formulation became a highly developed art under the Chinese, who were printing from hand-cut blocks in the eleventh century AD, 400 years before Gutenberg introduced movable type in Europe. Writing inks differ from printing inks in that the latter are generally applied to a substrate by means of a printing press. Printing inks as supplied to the graphic arts industry are used in much greater volume by far as compared to writing inks. This article is divided into a discussion of printing inks, followed by some miscellaneous categories of ink, including ink for ball-point pens, with which the greatest amount of ink writing is done. The number of printing-ink manufacturing establishments in the United States is approximately 270 including some 30 captive ink manufacturers. The value of the total printing-ink production in the United States was approximately $4.1 billion in 2002 (see also PRINTING PROCESSES).

2. Printing Inks

Printing ink is a mixture of coloring matter dispersed or dissolved in a vehicle or carrier, which forms a fluid or paste which can be printed on a substrate and dried. The colorants used are generally pigments, toners, dyes, or combinations of these materials, which are selected to provide the desired color contrast with the background on which the ink is printed. The vehicle used acts as a carrier for the colorant during the printing operation, and in most cases also serves to bind the colorant to the substrate. Printing inks are applied in thin films on many substrates such as paper, paper board, metal sheets and metallic foil, plastic films and molded plastic articles, textiles, and glass (see FILM AND SHEETING MATERIALS; PAPER). Printing inks can be designed to have decorative, protective, or communicative functions. In some cases, combinations of these functions are achieved.

There are many classes of printing ink, which vary considerably in physical appearance, composition, method of application, and drying mechanism. These also fall into three general types of consistency or viscosity, paste, liquid, and solid. The classes are letter press and lithographic (litho) inks, which are called paste inks, and flexographic (flexo), rotogravure (gravure) inks and jet inks, which are called liquid inks (1) examples of solid inks are electrographic toners and hot melt inks.

Table 1 gives typical properties of inks used in the various processes.

The four key properties of inks are drying, rheology, color, and end use properties. Use properties are those considerations that determine how printed substrates function throughout all processing and usage from the time of printing throughout the useful life of the printed product.

2.1. Drying.

Drying may be defined as any process that results in the transformation of a fluid-printing ink into a very high viscosity or solid film. An ink is considered dry when a print does not stick or transfer to another surface pressed into contact with it. Drying is accomplished by one or more of the following physical or chemical mechanisms: absorption, evaporation, precipitation, oxidation, polymerization, cold setting, gelation, and radiation curing.

Absorption. Some inks (eg, oil-based newspaper inks) dry by penetration or absorption into the pores of the printed stock, which has a blotter or sponge effect. This is accomplished by the gross penetration of the ink vehicle into the pores of the substrate, the partial separation of the vehicle from the pigment, and the diffusion of the vehicle throughout the paper. The ability of an ink to penetrate into paper depends on the number and size of the pores present in the paper, the affinity or receptivity of the stock for the ink, and the mobility of the ink.

Solvent Evaporation. Drying of ink by evaporation of solvent is generally achieved by application of heat and/or air flow and depends on the volatility of the solvent(s) employed in the ink formulation. Web offset and letterpress inks which dry by solvent evaporation are usually called heatset inks. Flexographic, rotogravure and jet inks usually contain more volatile solvents than heatset inks and may not require as much heat to dry. In either case, a balance must be maintained between satisfactory drying of the ink on the printed substrate and adequate press stability, or resistance to drying, in the ink distribution or delivery system of the printing press during the printing process.

Precipitation. An ink may also be caused to dry by precipitation of its binder rather than by evaporation of solvent. This can be accomplished by adding a diluent, such as water in the form of steam or humidity, to a hygroscopic solvent ink system, which causes the solubility of the resin in the ink film to decrease sharply and causes it to precipitate when its tolerance for the diluent is reached. Further drying is accomplished by absorption of the solvents into the stock and then by evaporation. Another form of precipitation setting is the quick-set mechanism. This utilizes resins held in solution in a relatively poor solvent, by means of a small amount of an excellent solvent (called a sweetener) blended with it. When the ink film is printed on the paper, an amount of the solvents is absorbed reducing the content of the sweetener solvent to a point which causes the resins to precipitate and the ink to set.

Oxidation. Inks that dry by oxidation behave much like oil paint films and dry by means of the reaction of drying oils (qv) with oxygen. They contain metallic driers, which catalyze the absorption of oxygen by the drying oil (see DRIERS AND METALLIC SOAPS; PAINT, ARCHITECTURAL).

Cold Setting. In this process, also called hot-melt, inks are applied to a substrate in a molten state and upon cooling form a dry ink film. Electrographic toners are powdered solids that are transferred from a charged plate to the paper, and then melted together to form an image which becomes solid as it cools. The electrographic printing process has grown significantly since its introduction in 1992. It is also the basis of operation of Xerographic copiers.

Gelation. Drying by gelation is accomplished by dispersing fine particles of a high molecular weight polymer, eg, poly(vinyl chloride) resin, in a latent plasticizer for the polymer. At room temperature, the dispersed polymer behaves like a pigment but at elevated temperatures it solvates, causing an immediate gel formation which is dry to the touch.

Polymerization. Thermal polymerization or curing of an ink film at elevated temperatures can follow many different chemical paths. Condensation and cross-linking reactions may be accomplished with or without the use of catalysts. However, this method of drying generally has not been widely used for printing inks, except those used for metal and glass decoration, and some clear coatings.

Radiation Curing. The use of radiation curing inks has grown significantly for a number of reasons. The continued concerns about volatile solvent, the desire to conserve energy, the marketing appeal of high gloss coatings, improved resistance to abrasion and chemicals, production efficiencies, and often improved press performances, have been several of the driving forces. Although there are several forms of radiant energy used in the printing industry to dry inks, only the use of ultraviolet (uv) light and electron beam (EB) energy actually cause curing of the ink or coating through a chemical change. Radiant energies such as infrared (ir) and microwave energies are also used, but these energies are used to heat the ink to drive off solvents and do not typically cause a curing (chemical change) of the ink. The use of uv and EB technologies has grown so that these curing techniques can be found in all printing methodologies: lithographic offset, letterpress, dry offset, flexographic, gravure, screen printing and jet ink printing.

uv Inks. The dominant system used for uv curing is based on acrylate chemistry and is cured through free-radical polymerization. The inks are composed of pigments, oligomers, reactive (acrylated) resins, monomers (often multifunctional), photoinitiators, and additives. The uv energy is absorbed by the combination of photoinitiators that generate the free radicals through cleavage, hydrogen abstraction or energy transfer. These initiator packages are designed to utilize the maximum amount of the uv spectrum that is available as well as provide fast and thorough curing. They are highly guarded proprietary secrets.

A second type of uv curing chemistry is used, employing cationic curing as opposed to free-radical polymerization. This technology uses vinyl ethers and epoxy resins for the oligomers, reactive resins, and monomers. The initiators form Lewis acids upon absorption of the uv energy and the acid causes cationic polymerization. Although this chemistry has improved adhesion and flexibility and offers lower viscosity compared to the typical acrylate system, the cationic chemistry is very sensitive to humidity conditions and amine contamination. Cationic curing is also slightly slower curing than the free-radical polymerization process. Both chemistries are used commercially.

EB Inks. EB inks are very similar to acrylic uv inks without the photoinitiators. The energy of the electron beam causes the acrylate double bonds to cleave directly, forming free radicals which initiate polymerization. Due to typically higher cross-linking and the absence of photoinitiators, the EB curing systems lend themselves to applications where very low odor, low off-taste, or low extraction or residual materials are important. EB coatings have been introduced that meet FDA requirements for direct food contact. EB systems must have an inert gas, eg, nitrogen, curing chamber since the free-radical chemistry is inhibited by oxygen. Also, if the curing chamber is not inerted, the electrons will react with oxygen to form ozone. Due to this inert gas atmosphere, EB applications are usually used for web printing where control of the amount of nitrogen is easier. Sheet systems do exist, but the mechanical difficulty of inerting usually precludes them. EB curing units are relatively costly compared to simple uv systems, but they require much less energy to operate, are insensitive to color and ink film thickness, and produce much less heat. EB units have seen significant reduction in pricing due to lower voltage units that require less shielding ($1,000,000 Ë $300,000). Due to the size and the cost, EB units are typically "end of press" applied while uv lamps can readily be installed between printing units on most multicolor presses. uv and EB inks are available for almost all the various applications and processes to be discussed in this article. Since the chemistry remains very similar (oligomer, monomer and photoinitiator (for uv)) further discussions are not given.

Infrared and Microwave Inks. These are inks which have been formulated to absorb these radiant energies. The energy causes the inks to heat and dry through the partial evaporation of solvent. Absorption of the ink into a porous substrate can also be part of the overall drying mechanism with these inks. They have not found wide commercial success due to the variability of the infrared absorption with ink color and the cost and energy inefficiency of microwave systems in drying inks.

2.2. Rheology. The rheology or flow of inks as they print or set is their primary physical property. In a Newtonian liquid, any stress produces a flow, and the rate of flow is proportional to the stress. But most inks are generally non-Newtonian and have a nonlinear flow curve. The common terms used to describe ink rheology are viscosity (resistance to flow); yield value (stress at which a liquid starts to flow); shear thinning (decreasing viscosity with increasing agitation); and shear thickening (opposite of shear thinning). Mayonnaise is an example of a material having a high yield value but a low viscosity (2–4). Ketchup is an example of a shear thinning fluid.

Liquid Inks. The ink-distribution systems of flexo and gravure printing presses are very simple, having few inking rollers, and do not provide the means to distribute and level highly viscous inks. Therefore, the viscosity must be low, on the order of 50–150 mPa · s (= cP). Yield value must be low also to permit distribution of ink from reservoir to fountain. Excessive shear thinning should also be avoided to obtain the best printability. Low viscosity ink is preferred for fine-line flexography and shallow-cell highlights in gravure printing.

Paste Inks. Letterpress and offset inks can vary in viscosity from 500 mPa · s (= cP) for a letterpress-type newspaper ink to over 100 Pa · s (1000 P) for special litho ink metal formulations. The viscous nature of letterpress and litho inks has caused press designers to use a multitude of rollers in the ink distribution unit to ensure uniform thin films and adequate transfer of ink to the printing plate. In addition to the importance of proper ink rheology as related to roller-to-plate transfer, it also controls, in large part, the fidelity of printing, drying speed, gloss, and overprinting properties obtained on the substrate. In most cases, higher press speeds require lower viscosity inks and vice versa.

Printing smooth, dense solids can best be achieved using somewhat higher viscosity ink.

Rheology is also an important color strength determinant. High pigmentation can lead to a high yield value, highly shear thinning ink, thereby forcing a compromise between color intensity and rheology.

Measurement. There are many types of instruments designed for measuring viscosity and other rheological properties of inks. These include capillary, orifice, rotational, and other types. Modern ink rheology measurements are made on instruments such as the Cone-Plate, Falling Rod, Rotational Torsion, and Efflux viscometers. Rotary Tackmeters such as the Inkometer and Tackoscope are also used to record tack (film splitting force) as well as ink misting and roller stability (see RHEOLOGICAL MEASUREMENTS).

2.3. Color and Coloring Materials. Another key property of all types of ink is color which may very well be the most important one to the consumer because it has such a great psychological impact. Color (qv) has three different attributes described as hue or shade, saturation or chroma, and lightness or value.

Pigments (qv) are used for color but also affect physical properties such as bulk, opacity, specific gravity, viscosity, yield value, and printing qualities. Different pigments of the same hue can have varying fade, heat, chemical, and bleed resistance (5,6). Judicious selection of pigment is also required, according to the use of the ink, in considering subsequent operations such as varnishing, waxing, lacquering, or laminating. The end use of the printed product also makes demands on the resistance properties of the colored pigments chosen. Inks also make use of inorganic pigments and of dyes, most commonly in the form of organic pigments, dyes rendered insoluble in one of a number of ways (see PIGMENTS, ORGANIC). Five dye families that are of interest to ink manufacturers are azo dyes (qv), triphenylmethane dyes (qv), anthraquinone dyes, vat dyes, and phthalocyanine compounds (qv) (see DYEING; DYES, ANTHRAQUINONE) (7,8).

Flushed Colors. Many pigments, although dry when purchased, are prepared in a water phase and are not wetted easily by nonaqueous phases. In a process known as flushing, pigment dispersions are prepared that obviate this difficulty. Phase transfer is generally accomplished by mixing the pigment in water presscake with a water-immiscible vehicle in a heavy-duty sigma blade (dough) mixer. Most of the water separates and can be easily removed, although complete dehydration requires further processing, usually heating under agitation in a vacuum.

Flushed colors generally result in higher gloss and color strength, and better rheology and easier use than their dry-pigment counterparts. In paste inks, they are the principal form of colorant used in the United States. In Europe, dry colors are still used because of the greater choice of vehicles available to the formulator, but the use of flushed color is growing as supplies become available.

Color Concentrates. In order to provide greater versatility and, at the same time, ease of use, pigment manufacturers also offer pigments in the form of color concentrates. These are liquids or pastes with 35–65% of pigment content. Pigments in this form are very well dispersed, requiring little extra mechanical effort to achieve the desired color value or fineness of grind. The concentrates often contain surfactants and/or resinous dispersants plus a solvent.

They are classified according to the solvent used. Easily dispersible (ED) pigments are produced by coating freshly precipitated pigment in a slurry tank with a resinous and/or monomeric dispersant and, eventually, drying and pulverizing the solids. Such pigments are also called stir-in, since they require minimum grinding effort in order to develop the full color value.

Toners are full strength undiluted pigments used to strengthen tinctorially weak batches of pigments. Occasionally, dyes are utilized as toners. The most common pigments used in ink manufacture are as follows.

Black Pigments. The only black pigment used to an appreciable extent in inks is carbon black. It is used in newsprinting, publication, commercial and packaging printing; in large quantities. Black pigments are offered in fluffy or beaded forms and in a variety of particle sizes and physical properties.

White Pigments. Opaque white pigments commonly used in inks, in order of decreasing opacity, are titanium dioxide and zinc oxide. TiO_2 is by far the most popular white pigment, because of its high hiding power. Mixtures of whites are often made with the various colored pigments to add opacity or to make pastel colors.

Transparent white pigments (extenders) commonly used in inks, in order of decreasing transparency, are alumina hydrate, magnesium carbonate, calcium carbonate, blanc fixe (precipitated barium sulfate), talc, and clay. Extenders are sometimes used to reduce the color strength and change the rheology and printability of inks. They can also be blended with TiO_2 in white inks, to reduce the overall cost.

Inorganic Color Pigments. Iron blue is made in several shades, such as Milori blue and Prussian blue. It is economical, but has poor alkali resistance. It is also used as a toner in some black inks.

Organic Color Pigments. Printing inks are the largest consumer of organic color pigments of any industry. They have bright, saturated colors and are available in a wide variety of hues and resistance properties, which makes them particularly suited for use in printing inks.

Yellow Pigments. Yellows consist mainly of diarylide yellows, Hansa yellows, and yellow lakes. Lakes are produced from dyes by depositing them on alumina hydrate. Hansa yellows are very strong and permanent pigments. They are resistant to many chemicals and are produced from azo dyes (qv) in a number of hues. Diarylide yellows, the most widely used yellow pigments, are very strong, usually not as fast to light as Hansa yellows, but more transparent. They are the universal choice for process yellows. Orange pigments include dianisidine orange, diarylide orange, and Persian orange lakes.

Red Pigments. There are more red pigments used than any other organic type and they range in shade from yellowish red to deep maroon and from dirty reds to very clean, brilliant reds. A few of the more common types are as follows. (*1*) The para reds and toluidines are fairly fast to light and semitransparent. They are used in poster and label inks. (*2*) The lithol reds are available in a wide range of shades with moderate permanency to light. (*3*) Lithol Rubine reds are universally used as magentas in all types of four-color process printing. (*4*) Rhodamine reds are brilliant and have good lightfastness, when laked with phosphotungstic (PTA) and/or phosphomolybdic (PMA) acids. They are extremely costly, and for this reason, are not widely used as process magentas, despite their favorable color. (*5*) Red Lake C is used for making clean, brilliant orange or warm red shades. (*6*) Watchung reds or Permanent Red 2B pigments are fairly clean and have fair bleed and product resistance. (*7*) Naphthol reds are relatively permanent and are soap-resistant. They are available in yellow and blue shades.

Blue Pigments. Phthalocyanine blues are the most widely used organic blues. They are available in both greenish and reddish shades. They have excellent lightfastness, excellent resistance to most chemicals, and are used as cyans in all four-color process printing. Victoria blue is a clean, red-shade royal blue. It is only moderately fast to light and finds most of its applications in packaging printing. Alkali blues of deep reddish shades find extensive use in all types of inks, often for toning black inks. Alkali blue toners are also supplied in flushed form.

Purple Pigments. Methyl violet is the most commonly used purple pigment. It is also widely used for toning black inks. In packaging, although very expensive, Carbazole and Vat violets are used where permanence and resistance properties are needed.

Green Pigments. Phthalocyanine green, the most widely used type, is a permanent and clean pigment. Some other organic greens, such as Malachite green, are used in packaging.

Daylight Fluorescent Pigments. These are used in all inks where brilliant fluorescent shades are required. The main applications are in packaging, greeting cards, wrapping paper, and posters. They generally are not very fast to light since they consist of dyed resins which are then pulverized to resemble a pigment.

Metallic Powders. These are usually either aluminum or bronze flakes and vary in shades from silver to gold, depending on the composition of the metal used. The silver powders can also be toned with organic pigments to produce golds or copper shades using transparent yellow or red pigments.

2.4. Other Ingredients. *Driers.* These are generally soaps of cobalt, manganese, and other metals formed with organic acids such as linoleic, naphthenic, and other organic acids. They catalyze oxidation of drying oils (qv), and thus are used in inks that dry by oxidation (see DRIERS AND METALLIC SOAPS).

Waxes. These are dispersions of polyethylenes, Fischer-Tropch, Teflon, or vegetable waxes (qv) in a vehicle or solvent. They impart slip and scuff resistance to ink films. Polyolefin waxes and Teflon are also available as powders that can be directly mixed into inks.

Antioxidants. Widely used antioxidants are eugenol, ionol, BHT, MEHQ and the like. They retard premature oxidation of inks on the press rollers when used at low concentrations.

Miscellaneous Additives. These include lubricants, surfactants, thickeners, gellants, defoamers, and preservatives.

3. Letterpress and Litho Newsprint Inks

The U.S. news ink industry, with a sales potential of over $490 million annually, represents a dynamic, ever-changing segment of the graphic arts market. Forces changing this industry stem from government regulations, shifts in market needs because of the growth of the electronic media, recurring shortages in petroleum-based raw materials, and novel technologies. In addition to these, the introduction of faster printing presses and new printing modes such as publication flexo further influence the evolution and change in ink technology.

Of the three printing modes currently available, the dominant web offset lithographic process continues to grow at the expense of letterpress printing. The change in the market share is governed by the growing demand for color and improved print quality, which the letterpress process cannot deliver. Water-based flexo has made some penetration of the newspaper market, but its growth has essentially plateaued.

The printing of newspapers is conducted at very high speeds, often reaching 3000 feet per minute. All three printing processes utilize similar quality newsprint which, essentially, is made of groundwood or thermomechanical pulp. Presses are fed a continuous web of newsprint that unwinds from a feed roller. Inks dry by absorption of liquid into the porosity of the substrate. Some evaporation of water in a flexo publication ink can accelerate the drying process.

3.1. Web Offset. Web offset is, by far, the dominant type of publication and commercial printing. Web offset lithographic printing uses planographic, aluminum-based printing plates, fountain solution, and an ink formulated to accept and emulsify water.

Lithographic inks are printed from planographic plates on which the image is neither raised nor depressed. The image is differentiated by a chemical difference from the nonimage area. In modern aluminum offset plates, the nonimage areas are anodized aluminum which has been chemically or mechanically roughened (grained). The image area is formed photographically or by direct laser imaging using a photopolymerizable or an ablative coating. An aqueous solution of salts, buffers, colloidal gums, surfactants, and other materials, known as a fountain solution, is used to prewet the nonimage areas of the plate and make them hydrophilic. The ink is then rolled over the entire plate, but since it is highly oleophilic it only adheres to the image areas which have been formed by the photopolymerized hydrophobic coating. This image is then transferred (offset) via a rubber blanket cylinder directly to the printing substrate or paper. The plates are relatively inexpensive and easily made, which is one of the big advantages of lithography. The ink must be able to emulsify some quantity of the fountain solution in a stable manner in order to have the ink transfer properly during this process. The interactions between the ink and the fountain solution thus become the critical factor in lithographic printing. It is important that proper formulation of the ink vehicle and fountain solution be done with a view toward controlling the surface chemistry of both ink and fountain solution, otherwise ink tends to deposit in the nonimage areas of the plate, causing scumming. The inks are formulated with resins and varnishes as well as surface-active additives to facilitate this emulsification process. Despite this apparent complexity, this process can yield excellent print quality when all three elements, ie, plates, fountain solution, and inks, are properly formulated and the printing parameters are maintained at optimum levels.

Web offset inks are somewhat highly pigmented, to yield the desired print density at a thin printing film ($\sim 1 \mu m$). The viscosity of offset inks is relatively high, but varies with the press configuration. A variety of additives are used to control the properties of wetting and dispersion of pigments, flow, lithography, and rub-off of inks. These additives belong to classes of materials such as surfactants, bentonite clays, alkyds, functional resins, polymers, etc.

3.2. Letterpress. This is also called typography, and is the oldest printing process still in use. It continues to be replaced by newer printing processes. Printing is conducted from a raised image area of the printing plate. Inks in the printing process are transferred directly from a raised area to a substrate. The printing plates contain a thick layer of photopolymer deposited over a plastic or aluminum base.

Basic raw materials for letterpress inks, such as vegetable oils, resins, and pigments, are essentially the same as those used in web offset inks. Inks are tinctorially weaker than offset, relatively fluid, and their low and high shear viscosities are lower than offset.

3.3. Flexography. The use of water-based flexographic ink for newspaper printing was initiated in the late 1970s. In comparison to letterpress or web offset printing, this is a relatively young printing process. The exclusion of oils from an ink vehicle lead to the elimination of undesirable strikethrough, with resulting brilliant colors. Despite its success in some areas of the market, this process still represents a small segment of the newspaper market (7–8% in 2003).

Printing is conducted with a typographic plate similar to letterpress. However, the chemistry of the photopolymer makes the plate water insensitive. A high quality of print has been demonstrated by newspapers utilizing this printing process. The printed matter is virtually smudge-free.

Typical inks are water-based, with acrylic emulsion resins as the main binder. Inks of this type occasionally use natural products such as starches, lignins, and lignin derivatives. Hence, ecologically, this process is more desirable. Press ready inks are very fluid and of low viscosity. Inks contain a variety of additives for the elimination of foaming, dispersion of pigments, rheological modifiers, slip agents, etc.

3.4. Web Offset Heat-Set Publication and Commercial Inks. Almost all heat-set inks are now printed on web offset presses, and are based on vehicles containing synthetic resins and/or some natural resins. These are dissolved in hydrocarbon solvent fractions which are specially fractionated for use in the ink industry. They vary in boiling range between 180 and 300°C. Small percentages of alkyd resins (qv) may be contained in these inks. They dry in less than one second by means of solvent evaporation in a heatset oven. These ovens utilize high velocity hot air to raise the web temperature to 120–150°C.

3.5. Sheet-Fed Offset Inks. A large segment of commercial printing is done on sheet-fed presses almost entirely by the litho process. Inks for these presses are based on vehicles containing phenolic modified, maleic-modified, or unmodified rosin-ester resins dissolved in vegetable drying oils and diluted with hydrocarbon solvents. Some inks also contain alkyds, which may be modified with other polymers, such as urethanes, styrene, and the like. On coated stocks, sheet-fed inks can be formulated to quick-set to a tack-free state by precipitation and solvent separation and then dry fully by oxidation. Air (oxygen) upon reacting with unsaturated oils forms a highly polymerized, tough ink film. The most commonly used oils are linseed, soya, and tall oils. Special acrylic resins have been developed for use in quickset inks, and offer nonskinning properties and excellent press stability.

3.6. Duplicator and Business Form Inks. Duplicator sheet-fed machines require very press-stable yet quicksetting inks. They must also possess good lithographic properties of wide tolerance for fountain solution and provide good printing properties on a wide variety of uncoated papers. The inks can contain drying oil alkyds along with hydrocarbon resins and high boiling (200–370°C) hydrocarbon solvents. Business form inks closely resemble the lithographic heatset or quickset inks. Business forms have also been printed by the ink jet method. These inks are usually based on water, glycols, and dyes.

3.7. Folding-Carton Inks. The majority of folding-carton inks are based on various quickset vehicles, as described above. However, when maximum gloss, good rub, and product resistance are required, they contain mainly oleoresinous vehicles. These vehicles are composed of phenolic, phenolic-modified, and maleic-modified and/or esterified rosin resins which have been dissolved in drying oils or alkyds or both. They dry by oxidation to form tough, glossy films. Hybrid uv curing inks that are capable of running on presses with conventional roller materials are finding growth in the sheetfed market. This allows a printer to run a high gloss uv coating over the hybrid uv drying ink in-line without glossing back as the uv coating would do if applied over a wet conventional ink. This process leads to significant reduction in process time and better economics.

3.8. Metal Container Inks. Ink vehicles for metal containers that are printed on special flat sheet-fed litho presses are based mainly on blends of oleoresinous varnishes containing alkyds, polyesters, and melamine resins. These inks dry during a 5–15 min cure at 150–250°C in long gas-fired ovens. Polymerization, oxidation, and cross-linking reactions accounts for their drying and hardening. Ultraviolet inks also have been used in metal decorating, but are not as popular in this type of printing.

Preformed Two-Piece Metal Containers. Ink vehicles for letterset printing of two-piece aluminum or steel containers are mainly based on special polyester vehicles used in conjunction with melamine cross-linkers. Short cycle ovens which dry inks in 1–5 seconds are now used and operate at temperatures as high as 350°C. The rheology of these inks must be adjusted to the unique geometry of the press. Desired rheological properties are achieved by the use of additives as well as extender pigments. Ultraviolet inks have also been used in this process.

3.9. Plastics. Vehicles in offset inks for plastics (polyethylene, polystyrene, vinyl) are based on hard drying oleoresinous varnishes which sometimes are diluted with hydrocarbon solvents. Letterset inks for polystyrene employ vehicles of somewhat more polar nature. Polyester or other synthetic resins (acrylic) dissolved in glycol ethers and/or esters are used in some of the older inks. uv inks are widely used for decoration of these preformed plastic containers. These inks are applied by letterset similar to the two-piece beverage containers.

3.10. Manufacture. Paste inks are produced in two ways: (*1*) by mixing predispersed (preground) or flushed pigment concentrates with vehicles, solvents, oils, and compounds, and filtering or (*2*) by mixing dry pigments or resin coated pigments with vehicles and compounds and then dispersing them with various types of ink mills. Mixing is done in small batch mixers, or in large agitated tanks which can hold up to 10,000 kg. A variety of equipment is being employed, from simple agitators to high speed, sawtooth blade mixers or concentric, double-blade mixers in order to achieve the desired predispersion. Milling can be done on three-roller horizontal or vertical mills and in media mills. The three-roller mill is still used for grinding small batches of viscous paste ink. Its steel rollers are polished and accurately machined to form a crown in the center. A speed differential exists in rotation of each of the rollers with respect to each other. They also can be set to provide greater or lesser clearance between them. The dispersion of the pigment is accomplished by shearing forces generated by this differential speed as well as by the closeness of roller setting. The shot mills break pigment particles by crushing action of the speeding shots. The smaller the size of the shot and the higher loading and the more complex (tortuous) path in the chamber, the better the dispersion. Inks may be heated so that they are low enough in viscosity to be ground in media mills (vertical and horizontal). Finished inks are packed in metal cans (0.5–5 kg), in metal or plastic pails (8, 11, and 19 L), or in 114- or 190-L metal or fiber drums, and for volume users, in large metal tote bins. The more fluid inks (news, flexo, or gravure) usually are delivered in tank trucks directly to the printer. Ink vehicles are usually produced in separate resin/varnish plants. Here 1,900–19,000-L reactor kettles are equipped with powerful agitators, reflux condensers, liquid traps, gas and liquid pumps, and ducts for material charge. Heating is done by multistage Dowtherm or hot-oil jackets, or in some installations, electric heaters. Temperatures and reaction rates are automatically monitored and controlled. Finished vehicles are filtered routinely via bag or cartridge filters. Synthesized resins can be cast or chipped in solid form from the reactor kettles and also converted directly into fluid varnishes in a single operation.

4. Flexographic, Rotogravure and Jet Inks

Flexo and gravure inks are both known as liquid inks because of their low viscosity. The inks for both systems have basic components in common with inks for other printing processes. Vehicles disperse and carry the pigment, and also contribute most to the end use properties. Colorants provide color. Solvents dissolve resins in the vehicle and determine drying rate. Additives modify ink properties to overcome deficiencies.

The vehicle is composed of resins, solvent, and additives. The resins impart adhesion and end use resistance properties to the film. Resins are polymers which can be film formers or nonfilm formers (Table 2). Film formers are flexible and form a continuous film when dry. Some resins require the use of an additive such as a placticizer to achieve film formation. Nonfilm formers are brittle polymers which do not form a film even with plasticizers (qv). Plasticizers are nonvolatile liquids or soft resins which may partially dissolve the main resins. Resins for flexo ink must be soluble in solvents which will not harm the printing plate. Resins for gravure ink do not have this handicap because of the metal gravure plate cylinder. Colorants are pigments or dyes. Pigments are chemical compounds which are insoluble in either the solvent or the resin. Because of this insolubility pigments must be mechanically dispersed into a vehicle and broken down to small particle size. The dispersion and grinding process is required to develop the color strength and keep the pigment stable in the vehicle. Dyes are chemical compounds which are soluble in either the solvent or the vehicle. Dyes give strong, brilliant colors compared to pigments but normally have poor resistance properties (to chemicals and light) as well as a potential to migrate. Solvents are required for two reasons. The first requirement a solvent must satisfy is to dissolve the resin; this results in a low viscosity ink suitable for printing. Secondly, the solvent must evaporate quickly and completely from the printed film.

Both flexo and gravure inks are delivered in the form of a virgin ink concentrate, which retards the speed of pigment settling and reduces shipping costs. (Note that this does not apply to uv or EB liquid inks since they do not normally contain any solvent and are used as received from the supplier). Solvent is used press-side to reduce the ink to a correct printing viscosity. One must choose the solvent carefully. A solvent which evaporates too quickly may dry on the flexo plate or plug up the gravure cylinder cells. A solvent which evaporates too slowly can result in too much retained solvent in the ink film, possibly causing odor, blocking, or resistance problems. In flexo and gravure printing, too slow an evaporation rate results in poor trapping of each subsequent wet ink. A commonly overlooked difficulty when dealing with solvent combinations is the relative evaporation rates of the two solvents. A solvent ratio in the ink of 50/50 does not necessarily evaporate from the ink fountain in the same ratio. If solvent lost by evaporation is replaced in the original ratio of 50/50, the solvent combination may be too strong (more of the slower evaporating solvent), resulting in retained solvent in the film or drying problems.

Additives are used to provide a specific property. For example, a wax provides rub resistance in the printed film or a special surfactant reduces foam generation in the fountain.

4.1. Manufacture. Manufacturing processes consist of two general operations, vehicle preparation and pigment dispersion. Vehicle preparation can be as basic as polymerization of resins or as simple as cold dissolving of vehicle solids in appropriate solvents. Therefore, vehicle preparation equipment includes autoclaves for polymerization reactions and high speed mixers for simple dissolving. Pigment dispersion can be done in a ball mill which lends itself to volatile fluid formulations, or in a vertical or horizontal media mill. Pebble mills using porcelain balls and linings are used for white and light colors because steel ball mills, although more effective, cause discoloration. Darker colors such as reds, blues, and blacks can be made in steel ball mills. Much of the pigment dispersion done currently is in a horizontal or vertical media or shot mill.

A premix of pigment and varnish is forced through a cylindrical cavity filled with mechanically agitated shot or ceramic media. The grinding takes place as the pigment clumps are forced through the small openings between the moving shot. Color concentrates are made in dough mixers and pigment resin dispersions, called chips, on two-roll rubber mills. These high shear methods often result in better dispersion and consequently higher gloss than is achieved with ball or media mills.

Rubber-mill chips are dissolved similarly to resins, to provide color concentrates. Dough mixer and chip concentrates must be diluted with solvent and other vehicles to make finished inks. Media milling is a method of choice in both flexo and gravure ink manufacturing. Other high speed dispersing units, such as the Morehouse, Cowles, Kady, and others, are also used.

4.2. Rotogravure Inks. Since there are no rubber or plastic components in contact with the solvents contained in gravure ink formulations, it is permissible to use more aggressive solvents such as ketones and aromatic hydrocarbons which cannot be tolerated in flexo inks. This provides the gravure ink formulator with much greater latitude in regard to binder selection. In other respects the compositions generally are similar.

Ink Types. Historically there are 10 gravure ink types categorized by the binders or solvents used: A, aliphatic hydrocarbon; B, aromatic hydrocarbon; C, nitrocellulose; D, polyamide resins; E, SS nitrocellulose; M, polystyrene; T, chlorinated rubber; V, vinyls; W, water-based; and X, miscellaneous. Many of these classifications are blurring as blends of the materials are becoming more common.

Solvents. Common terminologies used interchangeably are solvents, diluents, reducers, and thinners (Table 3). Technically, solvents are materials that completely dissolve resins in the ink vehicle. Diluents are liquids that may not completely dissolve the resin by itself. Solvents can also be thinners, but most often thinners are blends of solvents and diluents. Reducer is another name for thinner, referring to the solvent blends used to reduce the viscosity of a virgin ink on the press to running viscosity.

Solvents for A-type Gravure inks are aliphatic hydrocarbons, for example, hexane, textile spirits, Apco Thinner, lactane, VM & P (varnish makers' and painters') naphtha, and mineral spirits. Aromatic hydrocarbons such as toluene and xylene are solvents for B-type inks. Generally, a blend of aliphatic and aromatic hydrocarbons can be used for this type of ink, although the use of plain toluene is almost universal in publication gravure.

Ketones and esters are required for C-type inks. Types of esters are ethyl acetate, isopropyl acetate, normal propyl acetate, and butyl acetate. From the ketone class, acetone or methyl ethyl ketone (MEK) can be used. The usual solvent for D-type inks are mixtures of an alcohol, such as ethyl alcohol or isopropyl alcohol, with either aliphatic or aromatic hydrocarbons. Commonly used mixtures are 50/50 blends by volume of alcohol and aliphatic hydrocarbon.

The alcohols, proprietary denatured ethyl alcohol and isopropyl alcohol, are commonly used for E-type inks. Many E-type inks benefit from the addition of small amounts of ethyl acetate, MEK, or normal propyl acetate to the solvent blends. Aromatic hydrocarbon solvents are used for M-type inks. Polystyrene resins are used to reduce the cost of top lacquers. T-type inks are also reduced with aromatic hydrocarbons. Acrylic resins are used to achieve specific properties for V-type inks. Vehicles containing vinyl chloride and vinyl acetate copolymer resins make up the vinyl ink category. Ketones are commonly used solvents for these inks.

W-type inks use water, or mixtures of water and alcohol, as the solvent. Inks which are not of a recognized type are classified as X-type. The solvent required is specific to the ink formula and the ink maker makes proper recommendations.

Water-Based Inks. Approximately 50% of all flexographic inks use water as their primary solvent and diluent. These inks are mostly used on substrates such a paper, paper board, paper towels paper bags, corrugated boxes or other similar substrate where the absorbancy of the substrate can assist with the drying. They contain vehicles based on either acrylic emulsions, or hydrosols or an alkali-soluble rosin ester having a high acid number such as partially esterified fumurated rosin and shellac. Carboxylated acrylic polymers, usually containing some styrene, have largely replaced natural resins because they provide better abrasion and water resistance. Ammonia or other volatile amines are used to solubilize these carboxylated resins and form resin salts. The volatile alkali evaporates from the ink film, rendering the printed matter water resistant.

Main advantages of water inks include excellent press stability, printing quality, heat resistance, absence of fire hazard, and the convenience and economy of water for reduction and wash-up the main disadvantage of water inks is the increased energy required for drying, due to the high latent heat of water.

Applications of Gravure Inks. The majority of Type A and Type B inks are used for gift wraps, newspaper supplements, catalogues, advertising inserts, and similar publication work. Inks in the Type C group are used for printing on foil, paper, cellophane, paperboard, coated and uncoated paper, glassine, acetate, metallized paper, and some specialized fabrics. Type C inks are the dominant group used in packaging gravure. Type D inks have excellent adhesion to many plastic films. They are used in foil, paper, and paperboard as well as on a variety of films. Type E inks include a wide variety of inks and lacquers and some dye inks. They are often used on paper and paperboard, some grades of cellophane shellac, or nitrocellulose primed foil pouch stock glassine and many specialty coated papers and boards.

Extremely good resistance to alcohol and soap are two of the unique characteristics of Type T inks. They are regarded as high quality inks exhibiting high gloss excellent printability and heat resistance. Use of Type W gravure inks, primers, and lacquers has been motivated by the need to comply with VOC emission standards. Water inks are primarily used in packaging gravure on board and paper. Publication gravure printers are actively testing Type W inks for various publication applications. Type V inks are used for printing vinyl films and Saran.

4.3. Ink Jet Printing. This is a noncontact form of printing that has the advantage of including all the information on a printed page in digitized form in computer memory, thereby eliminating the need for a plate. There are several common types of ink jet engines (the device that applies the ink). One principle of operation involves the issuance of liquid ink from an orifice at very high speed to form a jet which is then broken up by ultrasonic energy to produce uniform droplets that can be charged electrically. These droplets can be deflected electrostatically into a catcher, while the uncharged droplets continue in flight to form dots on the printing surface to construct images. This is called continuous ink jet. Another principle of operation is the drop-on-demand, DOD, jet which emits droplets of ink only when energized by the computer. There are two methods for generating DOD droplets. One is the piezo technology and the other is the thermal technology. Piezo technology is currently the dominant form for commercial printing. Ink-jet technology provides a means of fast, dependable, quality, single or personalized copy printing. Its nonimpact nature permits printing on uneven surfaces and delicate materials. Computer operation permits the encoding of both repetitive and nonrepetitive information. Since the information sent to the ink jet is computer driven, the information can be changed from image to image, unlike other technologies. This allows for individual images and information to be printed for each print.

The inks formulated for jet printing must be very low in viscosity, stable, and free of any particles that could cause clogging of the jet nozzles, and be capable of depositing and adhering to a substrate with a minimum of character spreading or fogging. They are generally formulated with soluble dye or micronized pigment colorants in a suitable aqueous or solvent-based vehicle (9).

4.4. Lamination Inks. This class of ink is a specialized group. In addition to conforming to the constraints described for flexo and gravure inks, these inks must not interfere with the bond formed when two or more films, eg, polypropylene and polyethylene, are joined with the use of an adhesive in order to obtain a structure that provides resistance properties not found in a single film. Laminations are commonly used for food applications such as candy and food wrappers and snack bags. Resins used to make this type of ink cannot, therefore, exhibit any tendency to retain solvent vapor after the print has dried. Residual solvent would contaminate the packaged product making the product unsalable.

Even though high molecular weight polyamides are not nitrocellulose compatible (thereby eliminating the possible use of the commonly used nitrocellulose color bases) they do meet the requirements described previously and form the basis for most solvent-based laminating ink systems. High molecular weight polyamides disperse pigments well. A single color base line specifically for use in laminating ink can therefore be prepared.

In addition to polyamide, lamination inks ordinarily contain modifiers such as polyketone resin, plasticizer, and wax to impart specific properties such as block resistance and increased bond strength. Because laminating inks are usually reverse-side printed and end-up sandwiched between films, gloss is not a primary requirement. Water-base laminating inks that will meet the U.S. EPA emission requirements and have the correct functional properties are currently undergoing tests.

4.5. Screen Process Inks. These inks, often known in the past as silkscreen inks, are printed on the substrate by being forced through a screen stencil by means of a squeegee. For many years this was a hand-printing operation, but it has now become largely mechanized. High production speeds have been possible through the development of rotary screen technolgy which allows screen units be inserted in-line with other printing techniques on web fed combination presses. Screen-process inks are dispersions of pigments in vehicles which are, for the most part, solutions of resins in solvents of the boiling range of VM&P naphtha. Drying of solvent-based inks is usually by evaporation, but in some cases it is a combination of oxidation and evaporation. Various types of binders are used such as rosin esters, phenolics, cellulose derivatives, vinyls, and oleoresinous varnishes, depending on the film properties desired. uv inks are also widely used for screen-process printing. After premixing, the ink is ground on a three-roll or media mill. The resulting ink should be short and soft so as not to drag on the squeegee and to release the substrate cleanly after the print is made without excessive stringing.

The screen-process method of printing can apply a thicker film of ink to the substrate than other printing processes, and for this reason is particularly adapted to applications where maximum opacity is desired, or where fluorescent pigments are used, or for printing etch-resists for printed circuits. Screen-process printing also is used for printing of both board and paper posters, metal signs, glass, ceramics, cloth and plastics. The substrate need not be flat; the process also accommodates round or oval objects.

5. Miscellaneous Inks

5.1. Stamp-Pad Inks. These inks are impregnated into a cloth or foam rubber pad and transferred by pressure to rubber type which is then stamped or impressed against the substrate. The inks must be completely nondrying in the pad and yet dry by rapid penetration into the paper. Since it is desirable that the total ink soak into the stock, dyes are used rather than pigments. The vehicles used are usually glycols.

5.2. Ball-Point Inks. These inks are medium-viscosity semi-Newtonian fluids of high tinctorial strength which must be slow drying and free of particles so that they continue to feed to the paper without clogging. Drying on the paper is accomplished by rapid penetration and some evaporation. These properties are obtained by strong dye solutions and pigment dispersions in vehicles containing oleic acid and castor oil or a sulfonamide plasticizer. Rheology of these inks exhibits modest thixotropy which prevents their leakage through the openings around the ball.

5.3. Water-Based Writing Inks. These consist of very fine pigment dispersions in aqueous media containing small amounts of glycol or glycerol and a dispersing aid. They dry mainly by evaporation and quick wetting of cellulosic fibers in paper substrates.

5.4. Engraving Inks. Steel-plate printing is an intaglio process, or copper in which the image is etched or engraved in continuous nonscreened lines on a steel plate. The ink is applied in a heavy layer to fill the engraving and then wiped off the nonprinting surface with paper or a rotating plastic roller and a washing fluid, leaving the ink only in the engraving, which is then pressed against the paper with very high pressure to deposit the ink on the paper. This process is used for high quality stationery, stock certificates, and paper currency. Owing to the thick film that can be deposited (ca 10–40 μm), high strength formulations are not required, but the body of the ink is quite short so as to wipe cleanly from the plate. Drying is by a combination of oxidation or polymerization and by evaporation of solvent. The pigment, including a large percentage of colorless extender pigment, is dispersed on a three-roll mill in a vehicle composed of heat-bodied drying oil or oleoresinous vehicle, sometimes in combination with a resin–solvent type vehicle. Web engraving presses using heat or electron beam curing have been developed, but most currency printing still uses sheet fed presses. They use appropriate polymerizing vehicles. Owing to the thick film of ink deposited, sufficient flexibility must be present to prevent brittleness on handling.

5.5. Electrographic Inks. Electrographic printing is accomplished by causing charged colored particles to move in an electrostatic field to a substrate in the form of an image. The image may be formed by a screen stencil or by a gravure cylinder. One of the primary advantages of this process is its ability to print across gaps and thus without pressure. The ink, also called an electrographic toner, is a powder composed of pigment dispersed in a solid resin. The particles must have the proper electrical properties, particle-size range, and be free-flowing. After the image is deposited on the substrate, it is heat- or solvent-fused to a continuous film. Pigments and resins must be chosen to meet the application requirements and at the same time to satisfy the physical and chemical resistance requirements of the process (see ELECTROPHOTOGRAPHY).

5.6. Decal Inks. Decalcomania is a transfer method of printing. The design is first printed on a temporary base by lithography, letterpress, gravure, or screen process, depending on the detail and thickness of image desired. Usually the temporary base is paper which has been coated with a water-soluble material. The inks must dry completely on the surface by oxidation or solvent evaporation because the treated paper has no ink absorbency. After the initial printing, the design is transferred to the permanent substrate by direct contact and soaking with water. The formulation of decalcomania inks is governed by the particular printing process employed in printing the transfer paper. Decalcomanias for ceramics require pigments that may be heated to high temperatures. Further, most decalcomanias should use pigments that are fast to light because many are subsequently transferred to outdoor signs or to store windows. Vehicles consist of oleoresinous varnishes containing metallic driers or are resin–solvent types.

5.7. Heat Transfer Inks. Heat-transfer printing is similar to the decalcomania process in that the printing is first done on a temporary substrate, but heat is used as the transfer mechanism rather than water solubility. One type of heat -transfer ink is made with heat-fusible resins and waxes to be transferred to cloth. These inks should penetrate into the cloth and not be affected by subsequent washing of the fabric. In the packaging industry, labels are printed on a web of special coated paper by conventional printing such as gravure. This web is then fed to automatic labeling equipment. The relationship between the paper web and the ink is such that the ink is immediately released by heat and transferred to the surface of the package, such as a plastic bottle, to which it then adheres as a permanent label.

5.8. Heat Sublimation Inks. Another type of heat transfer ink is used for transfering sublimable dyes from preprinted paper substrates to various types of synthetic fabrics using high temperatures (typically 190–210°C). The inks can be either lithographic, flexographic, screen, jet or rotogravure. The inks are formulated with a sufficient content of a special dye which turns to a vapor when heated sufficiently. The dye vapors transfer to the fabric and bonds to it. Natural fibers such as cotton do not work well in this appication. The inks are preprinted on a coated paper of 65–90 pounds and dried. The paper is placed in close contact with the fabric and heated to transfer the image to the substrate.

6. Economic Aspects

The world ink industry has changed over the last 10 years. There has been consolidation, more competition, and globalization. Whereas the United States accounted for 32% of the world ink sales a decade ago, it has slid to 26% of the $\$14.4 \times 10^9$ industry. Western Europe accounts for $\$4.4 \times 10^9$ and the Far East accounts for $\$4.1 \times 10^9$ of the ink industry. These three regions account for 85% of the world market.

In the U.S., $\$3.25 \times 10^9$ worth of ink was produced in 2003 (down from previous years). The globalization and consolidation that has taken place over the last 10 years has resulted in several changes. Relative profitability in the U.S. has decreased due to competition both domestically and internationally. In 1992 60% of the production was accounted for by 10 producers whereas in 2003, only four companies make up this volume: SunChemical, Flint Ink, INX Sakata, and Color Converting. Table 4 gives data on the 2002 printing ink market.

7. Quality Control and Testing

Control of inks is done by examining their color strength, hue, tack, rheology, drying rate, stability, and product resistance. Elaborate control equipment and laboratory testing procedures are employed to test the finished inks. Weather-Ometers, Fade-Ometers, glossmeters, printability testers, colorimeters, spectrophotometers, viscometers, rub testers, and gas chromatographs are employed to check production batches or to pretest new submissions or raw materials. Proofing presses and sometimes pilot presses are utilized by ink manufacturers to control production and test new formulations. The move toward higher printing speeds and quality, and greater economy and reduced volatile organic compounds (VOCs), necessitates intensive ink research and development efforts. New regulations, availability and cost of raw materials, new or modified substrates, and faster presses require constant updating of the formulations. Considerable research and development time and expenditures have been devoted to low VOCs and low temperature drying inks. Ultraviolet light, electron beam, and water-based inks for various applications are some of the areas of research and development being actively pursued. Trends to a more universal use of renewable resources have led to increased amounts of natural products such as vegetable oils and rosin in litho inks of all types, particularly in sheet-fed litho inks.

8. Environmental Considerations and Regulatory Compliance

8.1. Overview. Since the ink industry is a specialty sector of the chemical industry, the focus of this section is generally limited to those regulations affecting the chemical industry. The federal regulations are the ones under the Environmental Protection Agency, (EPA), the department of labor (DOL), and to a lesser degree, the Food and Drug Administration (FDA). In addition there are some state and voluntary guidelines that also impact ink.

It is interesting to note that topics presented in the 4th ed. of Kirk are largely the same regulatory constraints that are faced by the ink industry today. The principal, reason for this is that, in the intervening years, there have been few new regulatory initiatives affecting this industry. While there are few new requirements, the emphasis has shifted to enforcement of the existing regulations and their impact on the newer business models of the first decade of the 21^{st} century.

In general, environmental concerns affect the several interfaces served by this industry. These include the ink manufacturing companies, the converting industry that uses the products to produce packaging and printed matter of all types and even extends to issues related to the ultimate end user companies whose printed or packaged products are often distributed world wide.

Common environmental aims such as reducing air pollution, use of renewable resources rather than crude-oil-based chemistries, biodegradable inks and coatings, the pressure to recycle waste materials back into the raw material supply, etc, all impact printing ink technology. Over the past twenty years, new ink products have been developed in response to these environmental concerns and will continue to emerge as new issues supplant existing ones.

The United States has been among the most highly regulated countries in the world. Beginning in the mid 1970s and continuing through the early 1990s, there was a persistent flow of legislation governing not only virtually all printing processes but the use and disposal of printed matter as well. A very clear historical account of the effect of antipollution laws on all aspects of printing can be traced. These laws have indirectly driven many changes in printing ink technology in order to accommodate concerns of the primary customers, the printers.

Since the late 1980s similar regulatory forces acing upon the Canadian, European and now Asian markets have been seen. However, the heightened perception of environmental problems is propelling these countries at a faster rate than has been the history in the United States. As printing ink supply becomes a global business, the successful marketing of ink technology now requires attention to an expanding body of world wide regulations.

United States regulations encompass both federal, state, and local guidelines. In addition, there are numerous voluntary industry guidelines affecting ink making. A brief review of the major regulations follows. The review is not comprehensive and is presented only as a reference source of the ink industry's responsibilities under the law.

8.2. United States Regulations. *Occupational Safety and Health Act (OSHA).* The federal OSHA regulation is a performance oriented standard administered under the Department of Labor and deals principally with physical aspects of safety and those things generally associated with accident prevention. The primary informational vehicle of the OSHA Hazard Communication Standard is the Material Safety Data Sheet (MSDS). The principal aim of the MSDS was originally based on the acute health effects of ink products used in the work place. However, as these efforts have matured, there is increasing emphasis on communicating long term health effects as well. The OSHA regulation also regulates the proper labeling of printing inks.

State Right to Know Laws (RTK). These state guidelines can be thought of as an extension of the federal OSHA requirements and primarily affect the labeling of printing inks in various states. Relatively few states have chosen to enact laws that have requirements greater than the federal OSHA guidelines. As an example, printing ink products shipped to converters in California, Pennsylvania, New Jersey and Massachusettes, require additional labeling and informtion.

Food and Drug Administration (FDA). FDA regulations deal with materials that are additives to food. They restrict both materials added directly to food and materials that can migrate into food from the direct contact with the packaging that contains it. Ink is rarely used directly on food; however these regulations constrain the kinds of chemistries of inks and coatings that may be used in direct contact with food. For the ink industry, the primary impact is packaging and the guidelines are based on a positive list of materials. Through the 1990s to the present time, concerns for materials that migrate to food has become an increasingly complex issue. This trend has made data on extractables in printed matter the basis for risk assessment of food contamination. This, in turn, has been an impetus to develop ink technologies that provide a reduction in such extractables for certain critical packaging applications.

Resource Conservation and Recovery Act (RCRA). RCRA is a mature federal regulation administrated under the Environmental Protection Agency (EPA). Its focus is on both the reduction of waste through recycling and the proper disposition of unusable waste from industrial processes. The primary effect on printing inks is solvents, which can be flammable, and ingredients in ink that can contribute to the presence of certain heavy metals. The correct interface is the safe disposal of waste inks, but is often confused with disposal of printed matter. The latter is essentially not effected by this regulation.

Consumer Product Safety Commission (CPSC). The federal CPSC only addressed the maximum allowable levels of lead in children's toys and toy packaging. However, outgrowths from these guidelines form the basis of the many voluntary, toy manufacturers' and fast food chains' guidelines limiting lead and other heavy metals associated with the decorating or packaging of their products. Some guidelines limit total metals present while many constrain allowable soluble metal content by one of several standard testing protocols. These issues have also emerged rapidly in Europe, Asia, and Canada. Unfortunately, there is little uniformity in the various guidelines. The number of metals, the amounts allowed and the criteria for measuring them differ. It is often necessary to know the country or area of the world where a product will be used to ensure conformity.

Coalition of Northeast Governors (CONEG). The CONEG model heavy-metal guideline can be thought of as an extension of the CPSC. It is implemented through state regulations and only limits consolidated total metal content of lead, chromium, mercury, and cadmium in a finished package to a combined maximum of 100 parts per million. The regulation is aimed at protecting the environment during the disposal of post-consumer waste.

Toxic Substances Control Act (TSCA). TSCA, a federal guideline, is now a mature regulation administrated under the Environmental Protection Agency (EPA). It focused on establishing knowledge and control of the distribution of various chemicals into the society at large. Its mandate was to establish and update a list known as the chemical inventory. The initial inventory of chemicals used in industry was created in the early 1980s and continues being updated to the present time. Essentially, all products that will be used in another industrial application leading to finished goods must be comprised of chemicals registered under this regulation. Any new chemical created must be reviewed under several criteria, approved by the EPA, and added to the inventory before it can be introduced into U.S. industry. The law does not apply to finished goods usually defined as consumer items.

Within the ink industry, conformity with this regulation requires that printing ink formulations only use raw materials that are on this TSCA inventory. Regulations such as this can constrain new ink technology because of the testing requirements, inventory registration processes/fees and the time frame required to list new chemicals. In the worst case, the approval process can take 180 days.

By the early 1990s similar regulations began emerging in Canada, the European Common Market, and many Asian rim countries as well. Presently there are inventories established in many countries around the world and the number continues to grow. Unfortunately, as yet there is no universality among the inventories. This further constrains the distribution of both established ink product lines and new ink technology outside the United States.

Clean Air Act Amendments (CAA). This mature federal regulation has its origins in the mid-1970s and is also administered under the EPA. The CAA defines the components of an ink formulation that are regarded as volatile organic compounds (VOCs). Solvent emissions from inks during the printing process are still considered to be a significant source of air pollution. This regulation continues to be the principal impetus to the introduction of ink technologies that offer alternatives to traditional solvent-based ink chemistries.

Clean Water Act (CWA). The CWA is now a fairly mature federal regulation that constrains all waste discharges to groundwater or waterways. Although not directly impacting printing ink making, these regulations pose an unexpected deterrent to some printers who would like to use new ink technologies. As mentioned previously, the regulatory pressure to reduce volatile solvents emissions from flexographic and gravure printing processes has been the driving force to produce an extensive, advanced ink technology based on water-based chemistry. At the printing production level, water-based systems offer ease of clean-up of presses and related equipment. Local sewage facilities have often been used for disposal of such press wash and ink waste. New stringent effluent guidelines can require pretreatment of press waste prior to discharge to sewage systems. This cost can be a drawback to some printing segments seeking to use water-based technologies.

8.3. Current Business Practices and the Regulatory Sector. Globalization of the ink industry's business model began in the late nineties. The larger sectors of the ink industry began acquiring smaller companies both inside and outside the U.S. in order to increase market share. In the same time period, new raw materials became increasingly available from outside the U.S. There continues to be an economic advantage to buying raw materials and semiformulated goods (flushes, dispersions, varnishes, etc) for ink manufacturing in the United States.

The ink industry's customer base, the multinational converters/end users, increasingly want consistent products for their global business interests. Finished inks can now be made in the U.S. with ingredients from both internal and foreign raw material suppliers and then distributed around the globe. However, this model of the ink industry runs into unexpected regulatory conflicts. There is now a need for all elements of the supply chain to be aware of the relevant regulations not only in the U.S., but in other parts of the world as well.

The situation is compounded by the fact that, while there are often similarities, there is no global universality of regulatory constraints on business. Ignorance of the differences can risk a passive noncompliance of the laws inside and outside the United States. This is a troubling aspect of any industry that moves from national to international product development and sales.

It is beyond the scope of this section to explore the differences among regulations country to country that affect the global model of the ink business. However, coping successfully requires a focus on some new concepts. They are briefly discussed in the following.

Quality Information. Even before the trend to globalization, the ink industry realized that the amount and character of the supporting regulatory information on products was changing. Examples are the data that is required to support MSDS under OSHA as well as the EPA regulations relative to air pollution and toxic substances control. As this trend evolved within the U.S. it was clear that generic chemical information of the contents of products would have to be replaced with discreet chemical information based on each product. This concept has been dubbed as "Chemical Accounting". Materials accounting based on individual formulations is also the critical element in attempting to cope with nonuniform global regulations.

Information Management. The previous section speaks to the development of universal documentation of chemical specific information for the U.S. and now the global market. Distribution of that information is also undergoing some changes in our new business models. As ink manufacturers grow, the distribution of increasing amounts of chemical data needs to be managed in the most cost effective manner.

From the customer prospective, they too need to manage the availability of all the regulatory data generated by ink manufacturers in an effective manner. The distribution and management of information now relies heavily on computerization. One example is the Internet, which is proving to be an interesting way to post and access both MSDS and other regulatory data relevant to ink products. Under the guidelines set forth by OSHA and the EPA, creating specific ink maker/individual customer, controlled sites is a secure replacement for distributing hard data.

Global Shipping. It is appropriate to explore this issue in some detail as a potential example of a global regulatory conflict. As mentioned earlier, the U.S. introduced the concept of the control of the distribution of chemicals in the late

1980s. It is a violation of the TSCA regulations to use a chemical in a product that is not on the inventory. Since the development of the U.S. inventory, there has been a proliferation of inventories in many countries around the world. It is because there is no universality of these chemical lists that moving raw materials or products around the world can cause regulatory risk to a company.

The successful negotiation of the various countries' inventories requires both knowledge of how to access those lists, and the chemical content of a formulation. It also infers the need to address the question of the inventories in some time frame before a shipment is made. This latter point adds a new dimension to global business practices that was not a part of earlier ways of doing business.

There is even a deeper issue. For those companies engaged in developing unique products for customer needs, it is often the case that the success of those developments may depend on one or two unique chemical compounds. It is now essential that the development process ensures that there is early knowledge of where that product is expected to be used in order to create a viable formulation.

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R. W. Bassemir
A. Bean
Sun Chemical Corporation

Table 1. **Typical Properties of Inks**

Process	Viscosity	Dried film thickness
offset lithography	4–80 Pa · s	0.7–1.5 um
flexography	50–500 mPa · s	1–3 um
gravure	40–300 mPa · s	3–8 um
letterpress	3–50 Pa · s	2–3 um
screen	1– 20 Pa · s	25–100 um
intaglio	10–100 Pa · s	10–40 um
ink jet	1–5 mPa · s	1–2 um

Table 2. **Resins for Flexographic and Rotogravure Ink Vehicles**

Resin	Flexography	Gravure	Film former
acrylic	+	+	yes
cellulosics	+	+	yes
chlorinated rubber		+	yes
epoxy	+	+	yes
nitrocellulose	+	+	yes
polyamide	+	+	yes
polyester	+	+	yes
polyketone	+	+	
polystyrene		+	yes
polyurethane	+	+	yes
rosin-based	+	+	
Saran		+	yes
shellac	+		yes
vinyl		+	yes

Table 3. **Commercially Used Flexography and Gravure Solvents**[a]

Solvent	Comparative drying time[b]	Boiling range,°C	Flash point,°C	Density at 20°C, g/L
		Alcohols		
methyl alcohol	10	64–65	16	791
ethyl alcohol, 99% anhydrous	18	75–80	18	791
ethyl alcohol, 95%	20	75–80	18	815
isopropyl alcohol, 99%	27	81–83	21	785
n-propyl alcohol	55	95–98	29	803
sec-butyl alcohol	63	99–100	29	801
isobutyl alcohol	77	106–109	39	801
n-butyl alcohol	125	116–119	46	809
		Aliphatic Naphthas[a]		
hexane	7	66–70	−18[c]	683
fast diluent naphtha	7	60–82	−18[c]	689
heptane (tolu-sol)	15	93–104	−18[c]	725
lacquer diluent	17	93–116	−1[c]	743
octane	31	102–110	−1	743
VM&P (varnish makers' and painters') naphtha	51	121–149	10	755
mineral spirits	600	154–204	38	779
		Aromatic Hydrocarbons[d]		
toluene	26	109–112	7	868
xylene	88	135–143	27	870
		Esters[e]		
methyl acetate, 80%	5	53–59	−1[c]	899
ethyl acetate, 88%	10	72–80	6	887
isopropyl acetate	12	84–90	16	869
n-propyl acetate	22	95–103	18	881
sec-butyl acetate	33	104–117	32	860
isobutyl acetate	36	110–119	31	863
n-butyl acetate	63	115–130	39	875
amyl acetate	100	120–150	47	863
Cellosolve acetate	330	145–165	49	971
		Glycol Ethers		
Dowanol PM	88	118–126	38	917
methyl Cellosolve	130	123–126	46	962
Cellosolve	190	132–137	54	928
butyl Cellosolve	1000	166–173	74	804
		Ketones[f]		
acetone	5	56–57	−9[c]	791
methyl ethyl ketone	11	78–81	−1[c]	804
methyl isobutyl ketone	37	114–117	24	801
methyl isoamyl ketone	150	143–146	43	813
cyclohexanone	270	130–173	54	944
		Nitroparaffin		
2-nitropropane	50	119–120	39	987

[a]Acceptable for flexography if used with buna rubber plates and rollers.
[b]The drying-time comparisons are based on the use of ethyl acetate as standard at 10. Acetone is about twice as fast as ethyl acetate and is listed as 5.
[c]At very low temperatures, flash-point determinations are inconsistent; flash occurs below the temperature shown.
[d]Cannot be used in flexo.
[e]Should not exceed 25% of flexography solvent.
[f]Flexography usage restricted to butyl rubber plates and rollers.

Table 4. **2002 Printing Ink Market**[a]

Category	$\$ \times 10^6$	$\# \times 10^6$
Lithographic	1,746	1,059
Flexographic	1,038	539
Gravure	568	579
Letterpress	116	148
Screen[b]	321	90
Other	285	

[a]Data from the 2003 *NAPIM State of the Industry Report*.
[b]Screen data from the September 2003 *Printing Ink U.S. 2002–2007* prepared by the Hull Co. of Greenwich, Conn.