Short Review on Printing Ink Technology to Prevent Counterfeit of the Products

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1. Introduction

Ink is one of the most common materials used in the production of a document. Although there are various types of writing and printing inks, chemical and instrumental techniques remain similar when attempting to characterize their basic components. Typically, the goal of such examinations is to determine the source of the manufacturer, compare questioned and known items, and ascertain when the document was produced and/or decipher alterations, erasures, and obliterations. Inks and paints offer the forensic analyst many characteristics to work with. Aside from their invaluable physical characteristics, such as layer structure and markings, inks and paints are amenable to all three general analytical techniques (optical, organic, and inorganic) that are useful for the analysis of colorants. Older wet chemical and destructive tests have given way to microscopic and instrumental analysis in most cases. Because comparison is at the heart of most forensic chemical analysis of paints and inks, libraries, databases, and other collections are vitally important for the analysis of colorants. The Royal Canadian Mounted Police maintains the PDQ (Paint Data Query) database of infrared spectra of automobile paints. To date, this collection includes data from more than 13,000 vehicles and has a library of more than 50,000 paint layers. The United States Secret Service maintains an ink library containing more than 9000 inks, toners, and inkjet inks. A Munsell color chart for paints is useful, as are reference spectra of dyes and pigments obtained by using a variety of instrumental techniques. For microscopy, a reference set of pigments is indispensable [1,2].

Writing inks were first manufactured in both ancient Egypt and China in about 2500 BC. These inks were composed of soot bound together with gums. This paste was formed into rods and dried, then mixed with water immediately before use. Printing was invented by the Chinese about 3000 years later. They used a mixture of colored earth, soot and plant matter for pigments, again mixed with gums for a binder. Colored inks were introduced in 1772 and drying agents were first used in the nineteenth century. Today's printing inks are composed of a pigment, a binder, a solvent and various additives such as drying and chelating agents. Inks have been designed to print on a wide range of surfaces from metals, plastics and fabrics through to papers. The various printing methods are all similar, in that the ink is applied to a plate / cylinder and this is applied to the surface to be printed. However, the plate / cylinder can be made of metal or rubber, and the image can be raised up above the surface of the plate, in the plane of the plate but chemically treated to attract the ink, or etched into the plate and the excess ink scraped off. Different inks are produced to suit these different conditions [3,4]. The origins of printing can be traced back several centuries. The first movable type, molded in clay, can be traced to China in the eleventh century, and wooden type appeared in China in the fourteenth century. In Europe, book production from wood blocks was seen early in the fifteenth century, and Gutenberg introduced cast metal type in the middle of the fifteenth century. These inventions were the basic of the original printing method, namely letterpress printing. As the first printing was a development from writing and drawing/painting, it was natural that the first printing inks would be based on writing inks and paints. They were composed of lampblack or colored minerals dispersed in water-soluble gum [5].

These were based upon vegetable oils such as linseed or nut oil, which were heated to increase their viscosity and fortified with natural resin; to accelerate drying, metal salts were added. The first clear records of compositions of printing inks date from the seventeenth century and are of this nature. Until the middle of the eighteenth century, printers made their own inks. When the specialist industry of ink manufacture began to develop, the ink supplied was little more than concentrated pigment dispersion. Any skilled printer considered that he was a craftsman and would modify the ink that he purchased with his own 'secret' additives to give the printing properties that he wanted. During the eighteenth century, there were many publications of printing ink formulations. They all followed the same basic composition but included the use of other vegetable oils and natural resins, gave more details about the pigments used and focused on the details of the manufacturing methods. Throughout this period, a significant hazard to the ink makers was in the heating of the various oils. Sore of the processing even required the hot oil to be ignited and then extinguish with a metal cover [6,7]. Gradually, the basic composition of letterpress and litho inks began to converge, with rosin-fortified linseed oil being the basis of most colored inks and resin oil or mineral oils being the basis of blacks. The difference between the inks for the two processes was minor, but important; the litho inks contained additives and had a substantially higher viscosity. The invention of phenol-formaldehyde resins and the introduction of oil-soluble formulations in the 1920s initiated the era of synthetic resin media. Then in 1936, petroleum distillates were introduced to create the two-phase quick-setting mechanism that is the basis of the majority of conventional letterpress and litho inks used today. The basic dyes still

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have limited use but modern inks are based upon synthetic pigments in a wide range of synthetic media dissolved in volatile solvents, such as industrial solvents, methylated spirits [8–10]. By the end of the eighteenth century, metal ‘doctor blades’ had been introduced to replace the wiping of the surplus ink with a cloth, but the inks remained the same. It was not until the end of the nineteenth century that the ‘liquid’ inks were introduced. The earliest of these were water-based and probably similar to theiline inks of the time. These were later abandoned in favor of inks containing hydrocarbon solvents and natural or synthetic resins. Screen printing is a small segment of the printing industry, for which the history is less well recorded. In the early days, no suitable inks were available for screen printing, and use was made of ordinary decorative paints. Modern screen printing inks are based on a wide range of synthetic resins and polymers in a range of solvents with suitable volatility [11,12].

2. Types of Ink

2.1 Lithographic (Offset) Inks

The broad spectrum of applications for lithography requires a wide variety of inks. Offset, letterpress, printing inks, dry toner, process inks, etc., print image. Newspaper offset (cold-set) printing inks are typically very simple. Blacks are carbon black in high-boiling mineral oil with asphaltic material. Such inks could consist of up to 70% mineral oil which in the past, might have contained up to 15% aromatic hydrocarbons. During the last decade, these mineral oils have been replaced with grades that have about 5% aromatics, of which less than 0.1% are polyyclic aromatic hydrocarbons. Colored inks generally have a soya bean oil vehicle instead of mineral oil. For recycling of newsprint, the ink must be removable and therefore these inks do not contain binders that undergo significant oxidative cross-linking. Heat-set web offset inks are designed to produce high-gloss printed images. They contain lower-boiling mineral oils that are removed as the printed roll (web) passes through a hot air oven. A typical formulation might be: organic pigments (15–25 wt.%), hard resins (25–35 wt.%), soft resins and drying oils (5–15 wt.%), mineral oil (b.p. 240–260 °C; 25–40 wt.%) and additives. Radiation-cured offset inks, which are based on acrylate or vinyl/ether monomers, are becoming very important in both sheet-fed and web offset processes. The printed substrate is exposed to UV radiation or an electron beam at the end of the press, and the inks set within a fraction of a second. To exclude the oil-based inks from the hydrophilic areas of the printing plate, all offset litho printing processes require water-based fountain or dampening solutions. These solutions are typically slightly acidic aqueous solutions (pH 3.5–5.5) containing small amounts of buffers, alcohol, surfactants, hydrophilic polymers (gum arabic or cellulose derivatives), complex agents (EDTA, ethylenediamine tetraacetic acid) and preservatives [13,14].

2.2 Letterpress Inks

While letterpress is being replaced by other printing processes, it is still used to a limited extent to produce newspapers, magazines, self-adhesive labels, packaging and other printed product. Letterpress news ink is similar to web offset inks used to print newspapers. Moisture-set inks have been used for food packaging printing and contain maleic or fumaric acid-modified resins or products modified with phenolics as binders in glycol solvents. The printed surface is treated with steam or a fine mist of water, and the water-insoluble acidic binders precipitate, setting the ink. Water-miscible inks maintain the stability of the ink through an organic base that evaporates or is neutralized to induce drying. A variety of other ink types have been used in letterpress printing, including heat-set, quick-set, water-washable and high-gloss inks [14].

2.3 Flexographic Inks

Flexographic inks are liquid inks, rather than pastes, and are designed to dry quickly primarily by evaporation. Both solvent- and water-based ink systems are used extensively in flexography. Common solvents in the solvent-based inks include the lower alcohols usually mixed with esters and sometimes small amounts of higher glycol ethers or aliphatic hydrocarbons to obtain optimum ink solubility, viscosity and drying speed. A wide variety of resins are used in solvent-based flexo inks, such as nitrocellulose, polyamides, cellulose esters, acrylics and various modified resins [15]. Although pigments are the most common colorants, there is some use of pigmments, which are more soluble in water than in oil-based inks. Because much of the flexographic printing is on non-absorbent flexible packaging, polypropylene and poly (vinyl chloride) ink additives may include plasticizers to promote formation of a flexible ink film and waxes to add rub resistance. For environmental reasons, the solvents in ink are being increasingly replaced by water. Approximately 50% of all flexographic inks have water as their primary solvent. Resins in these water-based formulations are generally acrylic acrylates or fumaric acid-modified resin or shellac, neutralized with ammonia or volatile amines, which evaporate from the printed substrate and thereby set the ink film. A typical water-based flexographic ink for paper or paperboard contains: organic pigments (12-15%), resins (10-25%) and additives (5-7%); the remainder is water. For printing on plastics, the ink usually contains a small amount of alcohol (2-5%) and more additives (6-10%) [16].

2.4 Gravure Inks

Gravure inks are similar to flexographic inks except that ketones and aromatic hydrocarbons can be used as solvents, providing much greater latitude in the selection of binders. In the United States, gravure inks are divided into 10 categories according to the type of binder or solvent. For example, aliphatic hydrocarbons (hexane, VM&P (varnish makers’ and painters’) naphtha, mineral spirits) are used mainly in type A, Band D inks; aromatic hydrocarbons (toluene, xylene) are used in types B, D, M and T; and alcohols (acetone) are used in liquid type C inks. A typical formulation might contain pigments (8-15 wt.%), resins (15-20 wt.%), solvent (60-70 wt.%) and additives (0.5–5 wt.%). ‘Packaging gravure’ does not use hydrocarbon solvents but rather uses esters and alcohols. For various packaging substrates, resins may include cellulose nitrate, maleic resins, acrylate resins, polyurethane resins and polyamide resins, or mixed polymers of vinyl chloride/vinyl acetate/vinyl alcohol. Plasticizers (phthalates, citrates, adipates) also may be required, especially with cellulose nitrate. Basic dyes are used occasionally, in addition to pigments, in gravure inks. More recently, water-based gravure inks with formulations very similar to the water-based flexographic inks, are finding increasing use in packaging gravure [3,16].

2.5 Screen Process Inks

Screen printing is a highly versatile process that can apply a thicker film of ink to the substrate than other printing processes. A wide range of ink formulations is available, depending on the substrate and the requirements for the printed product. Drying may be by evaporation, oxidation, radiation-curing or other processes. Any of the resin types found in litho, flexo and gravure inks may be used, and the solvents can be of almost any type as long as they evaporate at a suitable rate, which is slower than that required for flexo and gravure. Solvents (propylene glycol ethers, aromatic and aliphatic hydrocarbons and cyclohexacontane) typically have somewhat higher boiling points than those used in gravure printing, and inks are more viscous. Although newly introduced ink formulations are usually lead-free, screen printing is one process that still makes significant use of lead chromate pigments. The use of N-vinyl pyrrolidone in UV-cured inks has declined [3].

3. Ink Composition

All inks, in their basic form, are composed mainly of a colorant(s) suspended in a vehicle (solvents and resins). There are also other organic and inorganic ingredients that may be present in inks, which can include antioxidants, preservatives, wetting agents, lubricants, and trace elements, but these typically form a small fraction of the overall formulation. Nevertheless, their importance should not be discounted because it is possible that contamination of these components may otherwise similar inks to be discriminated. Before delving into the various analytical approaches for the examination and characterization of inks, it is necessary to gain an understanding of the major components [17]. Generally, inks mainly consist of colorants (dyes and/or pigments) and vehicles (solvents and resins), as well as a variety of other ingredients such as antioxidants, preservatives, and trace elements, which when combined are collectively considered the ink formulation. These characteristics are applicable to writing inks, stamp inks, inkjet inks, typewriter inks, and commercial printing processes that utilize inks, such as offset lithography, flexography, and intaglio. However, this description does not apply to dry toner – printing material commonly used in photocopiers, laser printers, and some basic facsimile and machines. Dry toner has a different composition to facilitate a markedly different process for printing a document and is discussed later. Thermal transfer printing applies to printing processes that utilize heat to produce an image by either physical or chemical means or by a combination of both. This technology has evolved in the past two decades with the advent of bar coding, retailer receipts, fax machines, event tickets, and the use of high mega pixel digital photography and

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3. Colorants

Colorants are a crucial part of all inks because without them, inks would not be discernible under visible light (approximately 380 to 780 nm). The molecular composition of the colorants will dictate how certain wavelengths of visible light are absorbed and reflected, thereby influencing their color. Depending on the vehicle and its interaction with the colorant, two types of colorants can be used: dyes and/or pigments. Dyes are generally considered to be compounds with highly conjugated resonance structures. Their molecular weights can vary from the low hundreds to the high thousands. Dyes can be classified according to their chemical structure or how they are applied to material. It is beyond our scope in this chapter to adequately review the various types of dyes. The most comprehensive volume regarding dye information is the Color Index, published by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. Dyes may be listed by their International Union of Pure and Applied Chemistry (IUPAC) name, Chemical Abstracts Services (CAS) number, or the Color Index (C.I.) name. The colour index divides dyes into a series of large groups: acid dyes, azoic dyes (monoazo-, diazo-, triazo-), basic dyes, developers dyes, direct dyes, disperse dyes, fluorescent brighteners, food dyes, ingrain dyes, leather dyes, mordant dyes, natural dyes, oxidation bases, phthalocyanine dyes, reactive dyes, reducing agents, solvent dyes, sulfur dyes, and vat dyes. These colorants are used in many industries to yield colors on an array of substrates. However, solvent dyes and pigments are the most commonly used colorants in writing instruments. Acid dyes and reactive dyes are also used, but less frequently. The molecular structures of a common phthalocyanine dye and a monoazo reactive dye are shown in Figs. 1-2 [19,20].

\[ \text{Fig. 1 Ink compositions with and without substrate} \]

\[ \text{Fig. 2 Molecular structures of copper phthalocyanine and a monoazo reactive dye} \]

The major distinguishing feature between dyes and pigments is that the latter consists of fine particles of insoluble material that are suspended in the vehicle. Pigments are generally considered more stable and long-lasting than dyes because pigments are less prone to photodecomposition and are insoluble in water. Their color can be derived from a series of resonance structures. Their molecular weights can vary from the low hundreds to the high thousands. Pigments can be classified according to their chemical structure or how they are applied to material. It is beyond our scope in this chapter to adequately review the various types of pigments. The most comprehensive volume regarding pigment information is the Color Index, published by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists. Pigments may be listed by their International Union of Pure and Applied Chemistry (IUPAC) name, Chemical Abstracts Services (CAS) number, or the Colour Index (C.I.) name. The colour index divides pigments into a series of large groups: organic pigments, toners, lakes, extended pigments, and inorganic pigments. Toners, lakes, and extended pigments are all precipitated from an aqueous solution in conjunction with some catalyst(s) [20].

3.2 Solvents

The fluid portion of ink that suspends and delivers the colorant to the substrate is known as the vehicle. Vehicles are necessary to carry the color from the cartridge to the paper. Once on the paper, the solvent undergoes a series of changes over a fixed period of time, causing the colorant to dry on the paper. Changes that occur to the solvent–ink mixture over time can include polymerization, evaporation, oxidation, or photodecomposition. These modifications to the original chemical composition of the ink have been the focus of methodologies that are employed when attempting to date a document. Although much of the specific information on each company’s ink formulations is proprietary, there are some standard chemicals that are used as vehicles. Glycols, alcohols, and water are the most commonly found solvents in use for pens today. 2-Phenoxethanol (2-PE), ethanol, 1-phenoxopropan-2-ol, benzyl alcohol, and many more solvents can also be used as vehicles. The choice of which solvent or solvents to use often relies on properties related to the writing instrument. The writing instrument type (e.g., fountain pen, ballpoint, felt-tip marker), composition of the ink cartridge, region of sale (e.g., dry, humid), and type of colorants and resins are all considerations when attempting to determine the type of solvent(s) to be used. The desired properties for a single formulation are often achieved through a combination of several vehicles. Other considerations, such as the solubility of the colorants in the vehicles, are also critical, since vehicles are the primary means of delivering the colorant to the substrate [21].

3.3 Resins and Additives

Resins, which can be natural or synthetic, are incorporated into inks to provide them with a desired viscosity and a means to bond the ink and the substrate as the inks dry. Normally, the resinous material is dissolved into the vehicle to create a solution in which colorants can be added. Phthalates, ketone resins, styrene-type resins, phenol-type resins, rosin-type resins, and poly(vinylpyrrolidones) are just a few plasticizers that find use in ink formulations as binding resins. Along with the resins, additives such as biocides, surfactants, lubricants, corrosion inhibitors, preservatives, buffers, and diluting agents are included in ink formulations to enhance properties of the ink. Thermal desorption and gas chromatography are used mass spectrometry (GS–MS) to characterize ballpoint pen inks [21].

4. Properties of ink

The rheological properties of inks must be compatible with available inkjet printing technology. The surface tension and viscosity of the ink determine the velocity, size, and stability of the ejected droplet and the shape of the droplets impinging on the substrate. The impingement shape establishes trace resolution and thickness, which ultimately determine the trace mechanical and electronic properties [22].

4.1 Surface Tension

Surface tension is the force acting on the surface of a liquid, tending to minimize the area of the surface; quantitatively, it is the force that appears when attempting to determine the type of solvent(s) to be used. The desired properties for a single formulation are often achieved through a combination of several vehicles. Other considerations, such as the solubility of the colorants in the vehicles, are also critical, since vehicles are the primary means of delivering the colorant to the substrate [21].

4.2 Viscosity

Viscosity is a measure of a fluid’s resistance to flow. It describes the internal friction of a moving fluid. A fluid with a large viscosity resists motion because its molecular interrelation gives a high internal friction. A
fluid with a low viscosity flows easily because its molecular interrelation results in very little friction when it is in motion. The viscometer makes use of the rate of flow of a certain volume fluid through a capillary tube of a given length. Times were recorded for the flow of distilled water or any other solvent from the upper graduation mark to the lower mark and then used for calculation of the viscometer constant k. The viscosity of the measured fluid was determined following the same procedures for the calibration: \( \eta = ktd \), where t is the flow time in seconds and d is the density of the measured fluid [22,25].

4.3 Density

Density is defined as weight per unit volume of a certain conductive ink, which varies within the range of 0.8 ~ 2.0 g/mL. Density is as significant as that of surface tension and viscosity on the generation and deflection control of the inkjet droplets [22].

4.4 Particle Suspension

Most current commercial pastes or inks include metal particles or flakes as the main conductive component. In our preliminary experiments, it was found that even particles as small as several microns in diameter could clog the inkjet orifice and then the printing process would then be forced to stop for cleanup. There is a tendency to apply Nano silver or gold colloids as conductive inks, which have less clogging problems and can be cured at a relatively low temperature to form continuous thin films on various substrates. In the current research, however, the formulation of a particle-free solution for inks is preferred to reduce cost and elongate shelf life. Inks with a surface tension on the order of 25-70 mN/m and a Newtonian viscosity of 1-10 mPa have been found to be most suitable. Most commercially available inks possess viscosities and surface tensions that exceed permitted levels, and thus do not allow droplet formation in the range of 30-100 \( \mu \)m in size using inkjet technology [24,25].

5. Security Ink as a Part of Anticounterfeiting Technology

Invisible ink, also known as security ink, is a substance used for writing, which is invisible either on application or soon thereafter, and which later on can be made visible by some means. These are majorly used in steganography, anti-counterfeiting features to documents and currency, authenticity indicators on packaging, brand protection and in classified communications. There is a wide variety of security printing inks. Based on the security principle the inks can be classified as follows. The security feature may differ and is only known to the designer of the same. Based on the requirement the security ink may be visible or invisible under normal light conditions. Below diagram explains how visible and invisible inks work. Basically in visible inks, the pigments suspended homogeneously in ink vehicle reflect and scatter incident white light making it visible to naked eyes. In contrast invisible inks carry either white pigments or not at all allowing the substrate do the reflection and scattering of incident light. Hence ink appearing invisible to naked eyes [26].

5.1 Optical Inks

**UV / Invisible Inks** – The ink glows in specific color when exposed to ultra violate light. These inks either have white pigments or are without pigments. UV / Invisible inks can be alcohol based or acetone based. Based on the application, the ink composition can be change. For example in a gravure press the UV ink is Alcohol based to achieve required viscosity of the gravure printing process and in invisible ink pens the ink is a re-acetone based. The composition of the ink can be controlled with additives to impact the response of the ink to a particular wavelength of ultra-violate or Infrared light. As the security feature is carried by the solvent these can be produced in multiple colors at low cost [27].

Optically variable inks – optically variable inks or OVI contain tiny flakes of special film which changes color as the viewing angle is varied. The result is an ink which changes color as the viewing angle is varied. They are very expensive inks and generally only used in small areas. A patent on new photosensitive OVI is registered in the name of Judith D. Auslander in 2004. The number 50 on US Dollar is printed in this type of ink [26,27].

5.2 Magnetic Inks

Security principle is the pigment used magnetic material, such as cobalt oxide or magnetic iron oxide pigment (Fe_{3}O_{4}) and iron oxide (Fe_{2}O_{3}). Security features is the application of the magnetic detector can detect the magnetic signal decoding. The technical requirements are less than the micron magnetic pigment to the needle-like crystals, the size and shape so that it easily in the magnetic field evenly arranged.

5.3 Heat Activated / Thermo-Chromic Inks

Heat reactive-irreversible ink is colorless when printed. It contains organic/inorganic substances that oxidize when heated turning brown. Milk, sugar, cobalt chloride are a few common examples of such. When exposed to heat, sharp color appears and does not disappear once the temperature is lowered. This feature helps protect documents or sealed envelopes from being tampered with by the use of steam or heat. For example, some banks use these inks on checks as a security measure. These heat-reactive formulations are made to either disappear or change colors at a trigger temperature of 88 °F (32 °C). Authentication is quick and easy. Simply rub the document in the protected area and if this reaction does not occur, you know there’s a problem [29].
inks. Common compounds used in these inks are Ammonia, developed by red cabbage water. Copper sulfate is developed by sodium iodide, sodium carbonate ammonium hydroxide or potassium ferricyanide. Lead nitrate, developed by sodium carbonate or potassium ferricyanide [29].

6. Conclusion

In the high demand of security and an the more creative counterfeiting methods for gaining fortune in an illegal way, our society should move to a higher level of security to any of the common day branches and try its best to protect the welfare of our products in order to preserve stable growth in markets. In this article, it is mentioned that the process of security features in high end products and the trends to its future development. A slight rise of production price but a greater security level stay one step ahead of criminals. Future trends in security printing are getting on the way with the new nanoprint technologies, printed electronics and revolutionary inventions in digital printing. These and many more are to become the new security printed features in order to protect the public from illegal activities and bring a more safe and secure future of printed documents.

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