

HISTORY AND CHEMISTRY OF INK- A REVIEW

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Article Received on
30 April 2014,
Revised on 26 May
2014,
Accepted on 20 Jun 2014

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ABSTRACT

The review explains the history of ink with special focus on its chemistry, development and recent advances. Art of writing developed in growing civilization with reformation. With the advancement of technology, writing instruments have been developed in a phase wise manner. Though quill, fountain, ball, felt and gel pen have been used and also still in use as writing tools, these varieties of pens also brought changes in ink chemistry. Ink is a liquid, semi liquid or solid material used for writing, painting or drawing by on a support. Throughout history, ink has been made many different colored juices

and extracts of plants and animals as well as synthetic materials. Ink for writing and printing dates back to 3200 B.C. when the Egyptians used a mixture of lampblack suspended in vegetable gum. Egyptians and the Greeks used iron oxide to make ink from about 2800 B.C. Ancient, Chinese were making red ink (from mercury sulphate) and black ink (from iron oxide) propylene glycol, propyl alcohol, toluene or glycol ethers. Other ingredients like, resins, preservatives and wetting agent are also added.

KEYWORDS: Quill, Lampblack, Mercury sulphate, Iron oxide.

INTRODUCTION

Art of writing developed in growing civilization with reformation. It is a skill by which a person expresses his thoughts, ideas, feelings and emotions. Writing ability makes the human being a pioneer of the ecological system and sets him apart of this world among animal kingdom. This is the only talent that makes a person immortal by his valuable views which

direct the society for their upliftment. Again, in advanced culture scripts, stamps, currencies, economic and legislation records, ledger and legendry etc. can only be possible by utilizing writing skills. ^[1] Writing comprises writing tools to make documentation using well distinguished language. Chemists, physicists, technologists provided writing tools like colorful inks, pens, brushes etc. to write on a substrate like paper, cloth, rock, wooden block, plastic or metal sheet etc. With the progress of technology, scientists invented superior tools in the modern society. Writing is an advanced mode to make the imagination to come true that one would arise, preserved, secured and stable documentation. To achieve this target magnetic, electric, electronic inks are arising which will provide certainly a step towards conservative society. With the advancement of technology, writing instruments have been developed in a phase wise manner.^[2]

Though quill, fountain, ball, felt and gel pen have been used and also still in use as writing tools, these varieties of pens also brought changes in ink chemistry.^[3] Ink is a liquid, semi liquid or solid material used for writing, painting or drawing by on a support. Ink designed for use in different writing instruments or printing methods have quite dissimilar components recipes for formulation of inks have been modified over the years. Chinese were the first to use inks, usually mixing lake colors and black pulverized stone, but the birth of real ink occurred in the third B.C. ^[4] Modern ink contains many substances aiming to improve ink characteristics. Chemically inks are a mixture and composed of colorant, a vehicle and additives.^[5-6] The colorants is either dyes or pigments in a vehicle either water or organic solvent containing additional ingredients include pH modifier, humectants to retard premature drying, polymeric resin to impart binding and allied properties, defoamer to regulate foam efficiency, wetting agents such as surfactants to control thickness and rheology, modifiers to control ink application, biocides and bacteriostatic to preserve ink from bacterial and fungal growth to impart fowl smelling.

On the basis of a colorant (dye or pigment) used, inks are classified as dye and pigmented inks. ^[7] Similarly vehicle (water or solvent) used to manufacture inks also categorized the inks as aqua based and solvent based inks. Pigmented inks contain other agents that ensure adhesion of the pigment to the surface and prevent it from being removed by mechanical abrasion. These materials are typically referred to as resin (in solvent based inks) or binding agent (in aqua based inks). Pigmented inks have an advantage that less ink need to be used to create the high intensity of color as pigment stays on the surface of paper. Dye based inks are

generally much stronger than pigmented ink and can produce much more color of a given density per unit of mass. Dye based inks are made with solvent that dry rapidly as they have a tendency to soak into paper. A disadvantage of dye based inks is that they can be more susceptible to fading, especially when exposed to ultraviolet radiation as in sunlight. [8] Carbon inks were commonly made from lamp black or soot and gum Arabic. Gum Arabic keeps the carbon particles in suspension and adhered to paper. The carbon particles do not adhere to paper. The carbon particles do not fade over time of carbon ink is that it is not harmful to the paper. Over time, the ink is chemically stable and therefore does not threaten the strength of the paper. Despite these benefits carbon ink is not the ideal ink for permanence and ease preservation. The permanence and ease smudge in humid environments and can be washed off an item. The best method of preserving documents written in carbon ink is to ensure it is stored in a dry environment. Recently carbon inks made from carbon nanotubes have been successfully created. They are similar in composition to the traditional inks in that they use a polymer to suspend the carbon nanotubes. These inks can electrically conductive patterns. [9]

Aniline dyes developed in 1920, extend the range of color, printing also application to plastic, fabrics and other substances, such dyes are frequently used in irremovable ink. Synthetic dyes are now used for printing inks.

General printing ink began marketing a soybeans based ink. Use of this kind of ink increased during 1990s the biodegradability of soy ink increased as the ratio of soy oil to pigment improved. Other advantages of soy ink to include capability to produce brighter colors, its extended mileage, its renew ability and the fact that recycling papers printed with soy ink seeks to be an increasingly popular choice of environmentally concerned publishers mixed with sumac tree sap. From 2000 B.C. the ancient roman's developed ink called "Encaustum" from which the world ink derived. [10-14]

Early varieties include Egyptian ink various natural dyes made from metals. The husk or outer covering of beans or seeds and sea creatures like the squid were also used. Pigmented inks contain other agents that ensure adhesion of the pigment to the surface and prevent it from being removed by mechanical abrasion. Pigmented inks are advantageous when printing on paper because the pigment stays on the surface of the paper. This is desirable because more ink on the surface means that less ink needs to be used to create the same intensity of color. [15]

Pigments are the main components of ink, containing the different colors. Color printing inks are made primarily with linseed oil, soyabean oil, or a heavy petroleum distillate as the solvents (vehicle) combined with organic pigments. The pigments are made up of salts of multi ring nitrogen containing compound, such as yellow lake, peacock blue, phthalocyanine green and diarylide orange. Inorganic pigments also are used in printing inks to a lesser extent e.g. chrome green (Cr_2O_3), Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) Cadmium yellow (CdS) and molybdate orange. The size of the pigment is very important for the ability to diffuse in the solution inks. ^[16]

Iron gall inks were first noted in seventeenth century. In seventeenth century Europeans made ink with a mixture of tannic acid from the bark salt a recipe that formed the basis for the blue and black inks still used today. About 1450, the printing press was first developed, printing inks press was first. Developed, printing inks were made of varnish or oil with lampblack added. The first patent for colored ink was granted in England in 1772. Invisible inks were developed in mid 1800s. These inks were usually milk, whey or sugar solution when exposed to heat or light turn brown and visible. In the nineteenth century, chemical agents were developed that allowed easier use of a wider range of pigments for colors.

Changes in ink chemistry over the years closely reflect developments in the instruments for ink coating, the pen and the printing machine. The ballpoint pen, the felt tip marker and the fiber tip pen have led to inks containing solvents as the proportions of the ink ingredients, the amount deposited on the paper and the composition of the corrosion is caused by two major degradation processes acid catalyzed hydrolysis and iron (II) – catalyzed oxidation of cellulose.

Inks are manufactured from a wide variety of substances that exhibit very different chemical behaviors. Ink designed for use in different writing instruments or printing methods have quite dissimilar components. Since the 1950s chromatographic and electrophoresis methods have played important notes in the analysis of ink, where compositional information may have bearing on the investigation of the counter fighting, fraud, forgery and other crimes. Techniques such as paper chromatography, electrophoresis, TLC, HPLC, GC, Gas electrophoresis and the relatively new technique of capillary electrophoresis have all been explored as possible avenues for the separation of components of inks. ^[17-20]

Modern ink application – Up until a few years ago consumers had very little interest in ink other than refills for their pens. Ink refilling services for printing cartridges are offered by large, official printing companies as well as smaller “unofficial” refill companies. But the great paperless society hasn’t begun to show itself yet people simply like paper too much. Today in developed nations, it is rare to find a residence or a business that does not have a printing capability.

DIFFERENT TYPES OF PRINTING INK

1. Slow drying ink – it takes long time to dry.
2. Wax - free inks – used in laser printer.
3. Transparent ink- The colors in this process are transparent.
4. Fluorescents inks – It is used to archive bright color.
5. Metallic ink – Metals used in inks.
6. Thermo chromic ink – It helps to detect temperature in moving part.
7. Magnetic ink - It incorporate certain magnetic material in the ink and are used in printing cheque books for efficient screening by cashiers.
8. Electronic ink- Electronic inks represent the latest development in inks that is expected to change the concept of printing itself. It is used in sign board.

INK INGREDIENTS

1. Pigment (organic and inorganic).
2. Dispersants (surfactant and polymers).
3. Resin or polymers improve binding, rheology and mechanical properties.
4. Humectants retard premature drying.
5. Defoamers and antifoaming agents.
6. Wetting agents enhance contact with the substrate.
7. p^H Modifiers.
8. Biocides and bacteriostatics.

The advent of personal computers, personal electronics and the internet may one day replace libraries full of printed books and periodically with electronic predicts. ^[21]

For example, electrophoresis inks that currently are being commercialized can be corrected, edited or updated if needed by momentarily applying an electric field and e-books with digital displays, something similar to a palmtop computer, may be in vogue in few years.

Dyes in ink

Older style writing inks such as in fountain pens use fluid water based dye system. Dye based inks can produce much more color of a given density per unit of mass. However, because dyes are dissolved in the liquid phase, they have a tendency to soak into paper. Thus making the ink less efficient and also potentially allowing the ink to bleed at the edges of an image, producing poor quality. To circumvent this problem dye based inks are made with solvents that dry rapidly or are used quick drying method of printing such as blowing hot air on the fresh print. Another technique involves coating the paper with a charged coating. If the dye has the opposite charge, it is attracted to and retained by this coating while the solvents soak into the paper. Cellulose the material that paper is made of, is naturally charged and so a compound that complexes with both the dye and the paper's surface will aid retention at the surface. Such a compound is commonly used in ink jet printing. A disadvantage of dye based inks is that they can be more susceptible to fading especially when exposed to UV radiation as in sunlight. ^[22]

Hybrid inks

In the recent years hybrid ink consisting of both dyes and pigmentation has been introduced to the market. These inks are being used in Epson printer. The hybrid dye / pigment ink is also referred to as archival ink. ^[22]

ANALYSIS OF INK

Document examiners have invented methods for the scientific examination and identification of writing inks. Lawyers in the private sector and government agencies at all levels are using the examination of inks as a means of establishing the authenticity or fraudulent nature of questioned documents. A number of techniques described by researchers and technologists for the analysis of ink are as follows

Chromatographic methods

The comparison of writing inks has been made possible by the introduction of chromatographic methods which impact on the detection of fraudulent documents. Subtle alterations to documents such as insurance claims, wills and tax returns can have significant financial implications and a prime concern of document examiners and ink chemists have become to assess when the document entries were made and to detect the alterations or additions to a document. Two inks can be compared by both chemical and physical

examinations by using different techniques such as paper and thin-layer chromatography and other modern methods. ^[14]

Paper chromatography and paper electrophoresis

These were very primitive techniques used for analyzing inks. Paper chromatography has been among the oldest destructive methods employed in ink analysis and has been used especially for organic dye based inks. Characteristics of inks has been achieved by traditional electrophoresis methods.

Thin-layer chromatography

Thin-layer chromatography (TLC) is one of the simplest and most widely used chromatographic techniques. In TLC the stationary phase is a layer of powdered materials adhering to a smooth support such as a glass plate, aluminum or plastic sheet. The samples are spotted on a line (the origin) which is drawn near the bottom of the plate. The plate is then placed in a nearly vertical position in a chamber contained a liquid or a mixture of liquids called the mobile phase. The mobile phase is allowed to migrate up the plate to a certain height. As it does so it moves the applied samples characteristic distances. The plate is then removed, dried, and observed under visible light, exposed to a UV light, or visualized by spraying with a chromatogenic agents which reacts with the separated samples to form colored products. ^[23-26] The retardation factor (R_f) of a compound under a certain set of chromatographic conditions is defined as the ratio of distance traveled by the compound to the distance traveled by the solvent front from the original spotted position. The R_f of a compound depends on the type of adsorbent and developing solvent and can be used to identify a compound. The density of the separated spot may be used to estimate the quantity or concentration of that compound. ^[31-33]

HPTLC

HPTLC had three advantages over the TLC including rapidity of development, increased sensitivity (smaller sample) and better quality of separation with greater reproducibility. ^[28]

Capillary electrophoresis

Capillary electrophoresis (CE) is one of the most important analytical techniques that can provide rapid, high-resolution separations of complex mixtures. ^[34]

Luminescence

Hardcastle et al has introduced a method to detect enhanced luminescence of ink components. [16]

Microspectrometry

Spectra of inks on paper by micro spectrometric analysis deviated from the Beer-Lambert law as a result of scattering and variations in the opacity of the paper both in the transmission and the reflectance modes and also as a result of bronzing in the reflection mode. [21-23] Fourier Transform Infrared (FTIR) spectrometry has been used in the past to study characteristics of inks. [26, 27]

Luminescence photography

In 1973, Kevern investigated the identification of inks by combining the techniques of thin-layer chromatography and luminescence photography. The luminescence photography offered a very sensitive method of spot detection from thin-layer chromatograms. [29]

Laser excitation and spectroscopy

In 1986, Sinor et al used lasers and optical spectroscopy for questioned document examination. In ink examination, inks could be distinguished visually via laser-induced fluorescence. [30]

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