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# Written Communication in Chemical Technology

## Introduction

Language is the currency of communication. People exchange thoughts and information through language. As a medium of communication, writing allows the perpetuation of thoughts and information. It enables us to study the past and to record the present that becomes history for future generations. With significant development of science and technology, the methods of written communication have also advanced. Starting from simple writing utensils to the electronic printers prevalent in offices and homes today, advancing science has produced new instruments for written communication. Chemical technology has contributed to the development of these instruments.

## Pencils

The word “pencil” means “an artist’s paint brush.” It comes from the Latin penicillum, meaning “paint brush[11].”

The origin of pencils dates back to 16th century England where a large deposit of graphite was discovered. Because chemistry was not highly advanced, the material was thought to be a form of the element lead (Pb), that had been used earlier to leave marks on papyrus, an early form of paper[16]. The black core of a pencil is still called “lead,” although we now know that this core does not contain any lead.

Because graphite is soft and brittle, it was made into a stick and wrapped with string or sheepskin[17]. Later, a wooden holder was carved containing a graphite stick, similar to the pencils we use today.

For common materials in daily use, we rarely ponder the basic principles of their mechanisms. The same holds for pencils. How do pencils work? How do pencils write on paper?

To explain how a pencil leaves traces on paper, we need to understand the structure of graphite. Graphite is made of numerous layers of carbon atoms oriented in a honeycomb-shaped lattice. Stacking these sheets, called graphene, shown in Fig. 1, makes graphite. The chemical bonds joining atoms in one plane are very strong and thus not easily broken. In contrast, the bonds between planes are weak. As we write, by pressing down and moving the graphite "lead" of a pencil across paper, we are transferring several layers of graphene onto paper through weak interlayer coupling[3].

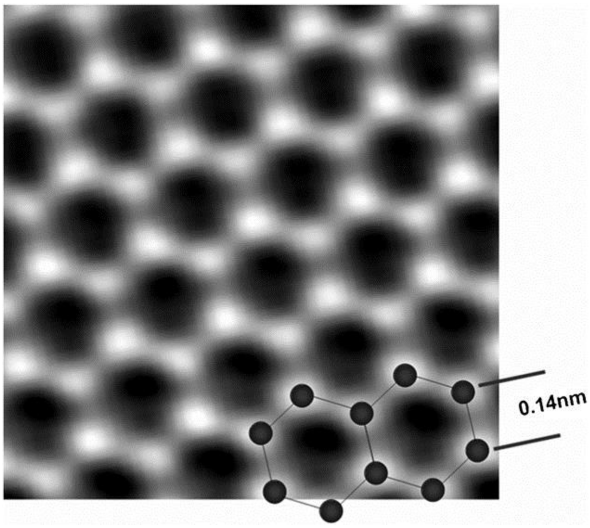



**Fig. 1. A Transmission-Electron-Microscopic Picture of Graphene with a Superimposed Schematic to Illustrate Structure**

(from Wikipedia[8])

Other than recording on paper, graphene has other potential uses, including "fabrication into products such as supertough composites, smart displays, and ultrafast transistors[7]." Although the term graphene first appeared in 1987 to describe the structure of layered graphite[8], it was only isolated in 2004 at the University of Manchester, England. Graphene is only one-atom thick but has a high crystal quality and is stable at room temperature. It is the thinnest of all materials, but it is strong and stiff. Also, it has potential for new componenets in electrical products because it is able to conduct electrons at room temperature faster than any other known material[7].

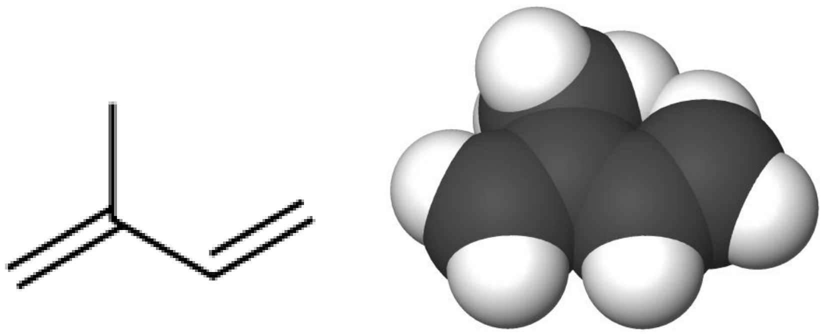
**Pencil erasers**

Since writing is not perfect, it needs editing. We often write, erase, rewrite, erase again, and rewrite again. How do erasers work?

Rubber erasers reverse the process of leaving traces of graphite on paper. They pick up graphite particles on paper because rubber is a stronger adhesive than paper[9].

Before rubber erasers were discovered, tablets of wax were used to remove lead or charcoal marks from paper[5]. Bread was also used. Rubber was often used to coat clothing, make balls, footwear, and bottles by people of Central and South America long before Europeans discovered the New World. In 1735, Charles de la Condamine, a French scientist, introduced a milky liquid from under the bark of a tropical tree to Europe. This substance, now known as latex, is used to produce natural rubber. Later in 1770, an English scientist, Joseph Priestley, named the substance “rubber” due to its ability to rub out pencil marks[22]. Rubber erasers were first produced in the same year by Edward Nairne, an English engineer, and were sold at the high cost of 3 shillings per half-inch cube[5]. However, rubber in its raw form would decompose. In 1839, Charles Goodyear showed that decomposition could be avoided by making rubber durable through a process called vulcanization, that is, mixing sulfur and lead oxide with latex in high-pressure steam. Vulcanization makes possible the production of erasers which we use today. What is the chemistry of this process?

Rubber is a polymer of many isoprene molecules, each with two carbon-carbon double bonds as shown in Fig. 2.



The white hemispheres represent hydrogen atoms and black balls represent carbon atoms.

**Fig. 2. Molecular Structure and Space-Filling Model of Isoprene**

(from Wikipedia[13])

As natural rubber, or latex, dries, the isoprene molecules form long strands. These strands are called polyisoprene. As latex dries more, polyisoprene strands stick together by forming electrostatic bonds, the bonds formed when one atom gains one or more electrons to become a negatively-charged ion and another atom loses electrons to become a positively-charged ion. This electrostatic force is analogous to two opposite poles of a magnet attracted to each other. The bonds between strands contribute to the elasticity of rubber, which allows rubber to stretch and recover. However, because the bonds between polyisoprene molecules are highly vulnerable to temperature changes, many scientists, including Goodyear, sought to find ways to make rubber more durable. Goodyear found that adding sulfur increased solidity of rubber because when rubber is heated with sulfur, sulfur attacks one of the double C-C bonds in isoprene and binds to the carbon atoms. Also, sulfur atoms bind to each other, forming disulfur bonds, and link again with carbon atoms in adjacent isoprene strands. This results in a netlike structure, ultimately making rubber harder and more durable, yet flexible[6]. Vulcanization (used to make rubber tires) enabled the production of the long-lasting erasers we use today.

**Ink**

We are often asked to use pens, not pencils, when signing documents. Ink marks last longer than pencil marks, although it is difficult to erase. Ink is also used in printers, which replace handwritten texts with printed material. How is ink different from graphite “lead” in pencils?

Many ancient cultures used ink to write and draw. Ink in ancient China dates back to the 12$^{th}$ century B.C., when the Chinese used substances including plant extracts, squid ink, and graphite mixed with water. In India, as early as the 4$^{th}$ century B.C., people used ink-containing burnt bones, tar, and pitch. In ancient Rome, a popular ink-making ingredient included iron salts, for example, ferrous sulfate (iron mixed with sulfuric acid). Iron salts were mixed with tannin from gallnuts and a thickener[12].

In modern ink, there are three main ingredients: the vehicle, pigments, and additives, such as surfactants and multifunctional polymers. The ink vehicle is a faint bluish-black solution that carries pigments. The two major types of vehicles are those from plants, such as linseed, rosin, wood oils, and those that are solvent-based, such as kerosene. On paper, the ink vehicle by itself is hard to read. Pigments make writing more legible[21]. Pigments generally refer to fine, solid particles that selectively absorb or scatter light at different wavelengths. Some examples of pigments are azo pigments, copper phthalocyanine blue, quinacridone, and diaryl pyrrolopyrrole (structures shown in Fig. 3)[14]. Azo pigments mainly reflect light in the range yellow to red orange[1], whereas copper phthalocyanine blue, as indicated in its name, shows a blue color. Quinacridone typically shows a deep red to violet color. The hue given by quinacridone is not only determined by the R-groups but also by the crystal form of the solid[19]. Lastly, diaryl pyrrolopyrrole, or DPP pigments, have shades of color in the range orange to medium and bluish reds[10].

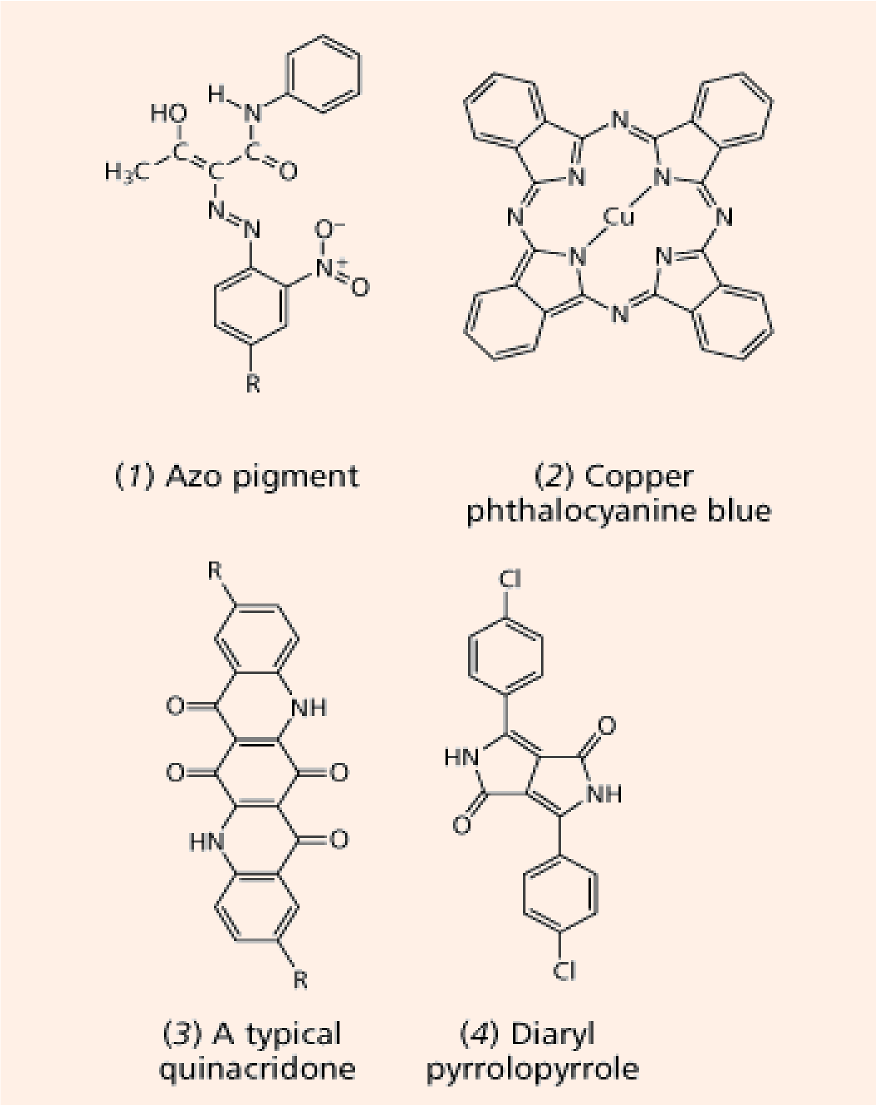


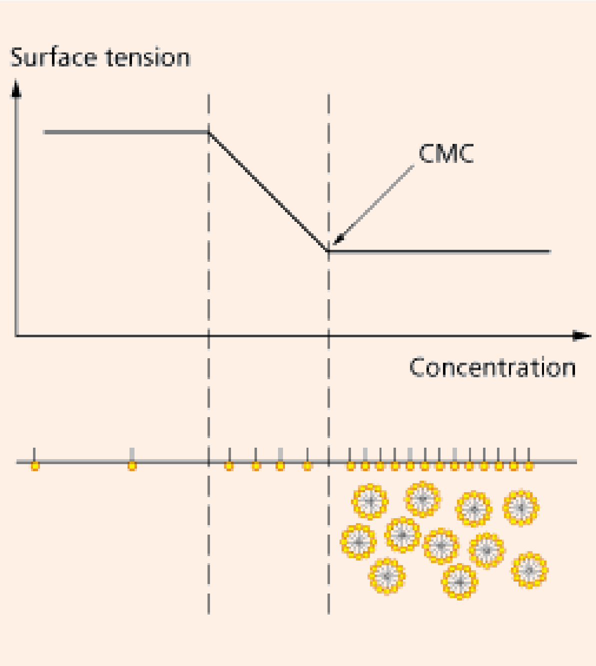

**Fig. 3. Structures of Common Pigments**

(from Ink Chemistry[14])

Additives, which include surfactants and multifunctional polymers, stabilize the mixture. They are used to fine-tune the properties of ink.

Surfactants stabilize a mixture for favorable pigment dispersion and also lower the surface tension of the solvent to enable ink to wet paper. Surfactant molecules contain hydrophobic hydrocarbon chains and a hydrophilic polar head group. There are different types of surfactants based on the polar groups. Those with ionic polar groups are called ionic surfactants. Examples include sodium dodecyl sulfate, or SDS ($CH_3(CH_2)_{11}OSO_3^-Na^+$ ) and cetyl trimethyl ammonium bromide, or CTAB ($C_{16}H_{33}(CH_3)_3N^+Br^-$).  For nonionic surfactants, an example is Dodecyl octaethyleneglycol monoether ($CH_3(CH_2)_{11}(OCH_2CH_2)_8OH$). Zwitterionic surfactants include *N*-*n*-Dodecyl-*N*,*N*-dimethyl betaine ($CH_3(CH_2)_{11}N^+(CH_3)_2CH_2COO^-$)[14].

Fig. 4 shows the effect of surfactants on the interaction between ink particles and the substrate (typically, paper).




As the concentration of a surfactant increases, some of the physical properties of the solution change sharply at a concentration called the critical micelle concentration (CMC).
Above the CMC, the surfactant molecules come together to form spherical aggregates (micelles) where the core is populated with hydrophobic chains and the corona by hydrophilic polar groups.

**Fig. 4. The Mechanism and Effect of a Surfactant on Ink**

(from Ink Chemistry[14])

Surfactant molecules aggregate on the surface of interacting layers to ease the application of ink onto paper by lowering the surface tension of the liquid mixture[25].

In addition to surfactants, some synthetic polymers are used to modify and tune the properties of ink. These polymers act as dispersants and also adjust the viscosity of the ink. For these purposes, some widely used polymers are nitrocellulose-based polymers and polyacrylates. Reactivity between polymers and other ingredients of ink determines some characteristics of ink, for example, viscosity and color strength[14].

The ink used in pens is different from that used in printers. Moreover, the properties of ink in ballpoint pens are different from those in rollerball pens.

**Pens**

The origin of pens can be traced back to 5000 B.C., when Indians used bird feathers and bamboo sticks to write. This is the origin of quill pens, using bird feathers, and reed pens that are cut from a reed or bamboo[15]. Both of these historic types of pens have a small reservoir of ink that takes up ink and that have tips that allow the ink to flow due to capillary action when in contact with paper. Capillary action refers to the flow of a liquid through a thin tube or through porous media[4]. Surfactants in ink increase the effects of capillary action by decreasing surface tension of the liquid to allow the ink to penetrate a solid surface[23].

Commonly used pens today include ballpoint pens and rollerball pens.

A ballpoint pen has a ball at the tip, kept in place by a socket between the ball and the ink reservoir of the pen, usually a long plastic tube containing ink. The ball is typically made from steel, brass, or tungsten carbide[15]. As the pen is used to write on paper, the ball rotates and lets ink flow out due to gravity[21]. Ballpoint pens use a viscous, oil-based ink that dries almost immediately when it contacts paper. This is one advantage of a ballpoint pen over a rollerball pen; it has free-flowing ink. Another advantage of viscous ink is that it does not leak easily. However, the disadvantage of the ballpoint pen is that the user has to apply more force, compared to when using a pen with free-flowing ink[2].

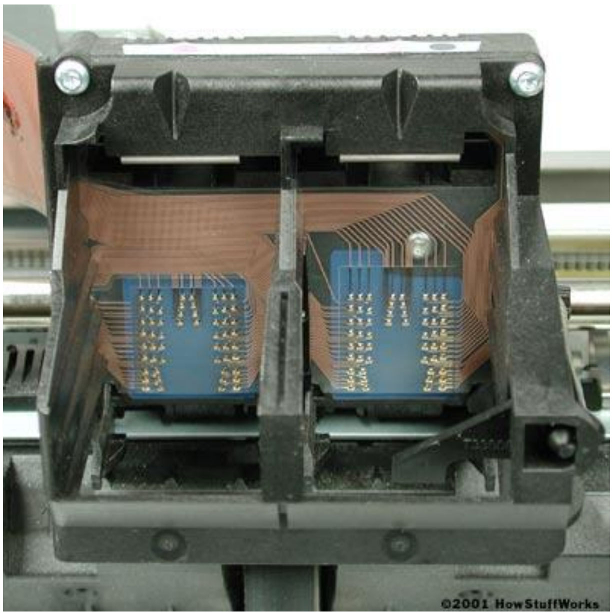
A rollerball pen combines the mechanism of the ballpoint pen with the traditional fountain pen that uses capillary action to release water-based liquid ink through the tip. It uses a less viscous water-based ink; thus, the ink flows more easily on paper. The advantages and disadvantages of using a rollerball pen are opposite to those using a ballpoint pen. It requires less force to write and allows the user to write more boldly, but it is more likely to leak and smudge since water-based ink dries more slowly than oil-based ink[20].

**Printers**

Today, instead of writing with pens and pencils, we often type and print. Printed materials are often more legible and neatly organized than those using a handwritten instrument. Printers require refill or replacement of ink cartridges. How is ink applied on paper in a printer?

Two major categories are impact and non-impact printers. Impact printers use a mechanism that requires direct contact with paper. In contrast, non-impact printers do not touch the paper when printing. Inkjet printers, the most widely used printers today, are non-impact printers[24].

Inkjet printers have a series of nozzles that spray tiny drops of ink onto paper. Fig. 5 shows the print head that contains these nozzles inside a printer.




The print head is the core of a printer. Using a belt and motor, it moves across paper to spray dots of ink on the surface. In the picture, the many small dots are the nozzles and the lines connected to them are the detectors that receive signals from the computer.

**Fig. 5. The Print Head of an Inkjet Printer** (from HowStuffWorks[24])

Two different technologies are used in printers to form droplets of ink: thermal and piezoelectric. The former, often referred to as the bubble jet, have tiny resistors that create heat and vaporize ink into bubbles. As the bubbles expand, the ink is pushed out of the nozzle and squirted on paper. Then, when the bubble pops, the resulting vacuum pulls in more ink into the print head. Figs. 6a and 6b illustrate the process. As the heating element creates heat, the ink (between the casing) vaporizes and is pushed out as shown in the last part of Fig. 6a.

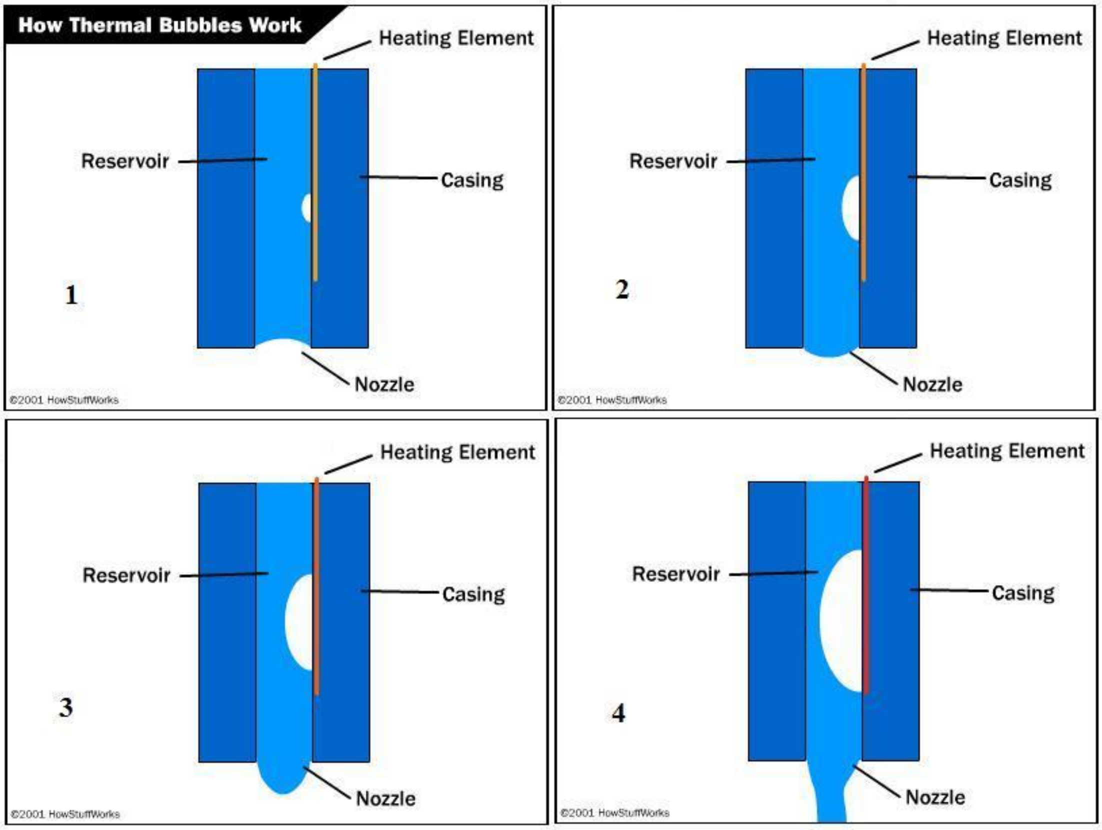



**Fig. 6a. How Thermal Bubbles Work to Spread Ink on Paper**

(from HowStuffWorks[24])

The vacuum inside the reservoir pulls ink from the cartridge. The last part of Fig. 6b shows the refilled ink reservoir and the cooled heating element.

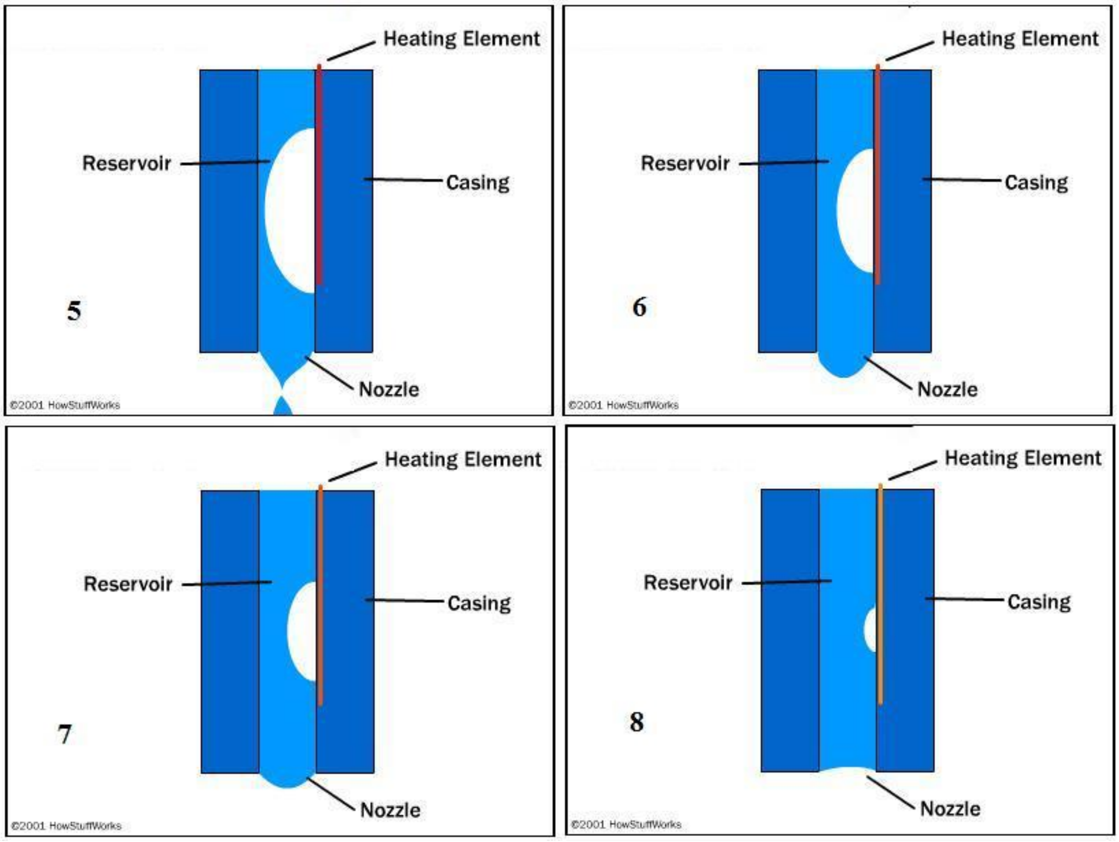



**Fig. 6b. How Thermal Bubbles Work (continued)**

(from HowStuffWorks[24])

The latter, piezoelectric, that uses piezo crystals, is patented by Epson. A crystal at the back of the ink reservoir of each nozzle receives electric charges that cause it to vibrate. When the crystal vibrates inward and outward, it forces ink out of the nozzle and then pulls ink into the reservoir to replace the ink sprayed, respectively.

**Conclusion**

From lead to graphene, from pieces of bread to vulcanized-rubber erasers, and from plant extracts to pigmented inks, chemistry has rendered writing more convenient. Advances in writing methods are directly related to advances in chemical technology. Understanding the properties of graphene and isolating it led to developing its potential for use in various technologies. Understanding the chemical reactivity of the molecules that constitute rubber and sulfur enabled the production of durable rubber. Understanding the principles of polarity and bonding in a liquid-ink mixture led to inventions of different types of ink, according to different compositions of surfactants and other chemical additives including pigments. Coloring pigments can be understood by the pigments' photon absorbance levels at different wavelengths of light. Novel discoveries continue this day. For example, inkless printers[18] have the advantage of reusing paper and not having to refill ink. Progress in chemistry and chemical technology continue toward finding new methods for written communication.

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