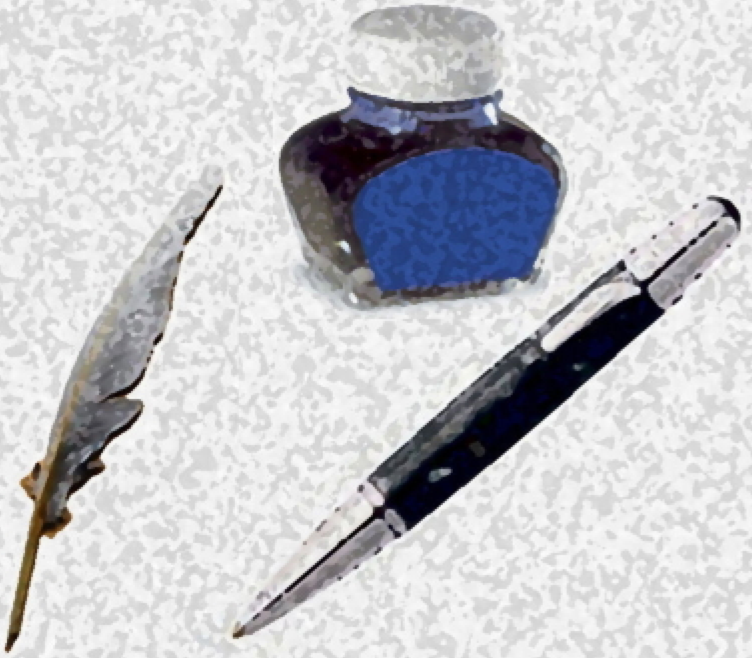
Alessandro Gusmano

Storia degli antichi inchiostri per scrittura e per stampa

歷代書寫及印刷墨水之變遷

Writing and printing inks through the ages



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Writing and printing inks through the ages

In memoria di Michelangelo Gippa
ed in celebrazione dei nostri primi 30 anni

In memory of Michelangelo Gippa
and for the celebration of our first 30 years

Table of Contents

…voice hath not utter'd,
Nor ink hath written, nor in fantasy
Was e'er conceived.
Dante, Paradiso Canto 19, 8-10

Introduction

Writing – which includes all types of grapheme, ideogram, pictogram or painted symbol – has produced documents that make up the historical, spiritual and scientific heritage of mankind.
The development of better and better inks has enabled writing to become history's major method of communication.
For many centuries, *graphemes* (meaning any kind of graphic symbol) were inscribed in stone and on tablets of clay or other materials; later, they were written using appropriate optical contrast media – inks – on substrates produced from plants such as papyrus, bamboo and the like, or of animal origin, like the various types of parchment and vellum. Over the last ten centuries or so, that complex vegetal and mineral system we know as paper has been far and away the most common material for writing.
The main properties that the makers of writing inks have striven to achieve over many thousands of years include color, flowability, adhesion and penetrability into the substrate, dryability and fastness or durability; in addition, inks must be odorless and nontoxic, and must not corrode the materials they are applied to.

From the mid-fifteenth century and the invention of movable type, the printing industry (though it existed in embryonic form even earlier) has spurred the development of new ink formulations, and the growth of "ink-based" communication has been exponential.
The historic and technological evolution of inks is something the public at large knows very little about: though inks have documented everything, precious few publications have attempted to describe their origins and their history for a general audience. Even this review can lay no claim to covering all of the studies and investigations that have been devoted to the topic, which because of their unavoidably technical nature are difficult for the non-specialist to understand.

1. General

Archeology shows that writing began with inscriptions scratched into the surface of stone, clay or wax tablets, and bark. Obviously, these forms of expression did not require “optical contrast” media, because the fact that they were inscribed ensured a clear contrast between the signs – the graphics – to be read – and the surface they were cut into.
With the introduction of new materials such as papyrus, parchment and, later, paper, that could not be inscribed, writing became a question of depositing contrast materials on the surface using brushes, reeds, pens and similar means.
Ink, the generic term for these contrast materials, comes from the Greek *enckauston*, meaning *burnt, cooked*, perhaps alluding to lampblack, the main source of black pigments in ancient times, which was produced by burning resinous woods and vegetable and animal waste in metal recipients over which terracotta (and later metal) cones were suspended. Smoke was collected in these cones, so that soot - consisting primarily of carbon – was deposited on their inner surfaces in the form of powdery particles of varying fineness.
Writing inks are thus preparations, generally liquid, which make it possible to apply markings to paper or other suitable materials that show good optical contrast with the substrate because they absorb more light than it does, and are thus darker – black, brown or some other color – and readily legible.

The solid components of inks (and of paints and lacquers) are called *pigments*: particles or grains whose composition remains unchanged during the writing or printing process, and even after drying. In ancient times, pigments were produced by grinding minerals and native earths; blue from lapis lazuli, red from cinnabar, yellow from realgar, green from malachite, and various tones of brown from earths such as Siena – or Sienna, as the pigment is often known – and other naturally occurring soils and clays (Figures 1,2,3,4,5).
The fluid that holds the pigment in suspension in the ink is called the *vehicle* or *binder*: the vehicle’s function is to transfer the pigment from the writing implement or forme – as the typeset page ready for printing is called – to the paper, and then to bind the pigment to the paper.

Dyes are natural or synthetic substances that are dissolved in the vehicle to produce colored inks of varying hue and saturation. The major types, which can be mixed to yield an enormous range of colors, are red-orange, blue and yellow dyes.

Important water-soluble red-orange vegetable dyes include *alizarin*, as well as *purpurin*, both contained in the roots of the madder plant (*Rubia tinctorum*), a herbaceous perennial (Figures 6,7,8). In Asia, the use of madder root as a dyestuff dates back to extremely ancient times, while the Egyptians used it to dye fabrics at least as early as 1600 BC.
To produce the dye, the madder roots are dried and ground into powder, which will keep for several years.
Another dye in the red-orange group, *heamatein,* is extracted from a leguminous tree, the logwood or *Haematoxylon campechianum*, which grows in South and Central America. It is also called *campeachy* because this plant originates around Mexico’s Campeche Bay. The dye is extracted by grinding the bark.

Among blue dyes, indigo was extracted from *Polygonum tinctorium*, or dyer’s knotweed, a herbaceous annual. Indigo can also be extracted from the biennial *Isatis tinctoria*, or *woad*, using the leaves from first-year plants. A closely related species, *Isatis indigotica* Fort. (*Chinese woad* or *tein-cheing*), can also be used for the purpose (Figures 9,10,11,12,13).

Yellow dyes can be extracted from *Reseda luteola* (*mignonette, weld* or *dyer's rocket*), a fragrant herbaceous plant containing *luteolin*, a highly resistant long-lasting deep yellow coloring agent that has been used since prehistoric times, especially for dyeing textile fibers and for silk in particular (Figures 14,15,16).

1.1 Ancient Chinese ink making

According to some historians, the origin of writing fluids dates to the third millenium BC, when we are told that an ink was invented in China by Tien Tcheu, who lived during the reign of the emperor Hwangti (around 2500 BC). As the annalist Chao-Shwo-chi (approximately 1000 BC) writes, the ink sticks – "writing lacquer" – then in use were made of animal glue and lampblack, pounded in a mortar until it became a very fine powder. In this period, the quality of these lacquer soot inks was regarded as so important that it was even controlled by a government inspector.
Huang Tsung, emperor from 713 to 755 AD, was an enthusiastic maker of inks, but the most celebrated figure by far was Tsu-Min, an inspector during the Tang dynasty: his fame was so great that his name is to be found in ink recipes as late as the fourteenth century.

Another legend would have it that in 620 BC, a Korean king presented several sticks of this lacquer to the emperor of China, but no documentary evidence supports this story.

The first certain formula, described in the book *Tsi Min Jao Shu* by Kia-se-che (fifth or sixth century AD) for preparing inks was based on an oily vehicle. The text, which has come down to us incomplete, gives the proportions for mixing lampblack with this oil.

Later research has named one Wein Tsu, between the third and fifth century AD, as the inventor of this formula.

This permanent ink was produced from lampblack (soot from wood smoke), bound with animal glue made from skins and hides, and then mixed with sesame oil or tung oil (from the tung tree, Aleurite fordii). Some very high quality inks included additives such as Borneo camphor or even gold dust, which scented the ink and gave a special gleam to the writing.

To produce lampblack, the Chinese burned resinous woods such as fir or pine in an atmosphere with very little air, as well as substances such as animal fats and gelatin, pitch, grape vines, resin, and certain types of seed. Combustion took place in wick lamps placed inside large terracotta containers (with small holes to produce a draft) topped by earthenware cones containing a bowl of water (for cooling) in which the dense smoke was collected, forming a fine, light, velvety powder. This powder was mixed with liquid binders featuring varying degrees of viscosity in a suspension that could be used for writing.

To make the classic Chinese ink sticks, the lampblack prepared as we have just described was ground and made into a paste by adding hot glue. This paste was then rolled into small balls, which were wrapped in a cloth and heated over steam for fifteen minutes. The next operation consisted of shaking these balls in the vehicle (the glue) to distribute the pigment (the lampblack); the longer this was done, the higher the quality of the resulting product. At this point, a solution of camphor or of camphor and rosewater was added which penetrated into the balls and softened them a bit so that they could be modeled into sticks. Once dried, the sticks were stored in a dry place, as moisture would have softened the glue and caused them to crumble.
Inscriptions on the most ancient ink sticks testify to the care with which they were made: "Light glue, 10,000 pestle strokes... or 100,000 strokes!" Though the most highly

prized ink came from southern Anhui, from the She district (She Xian) near Huang Shan (Yellow Mountain), where resinous pines and fir trees grow, the ink from Huizhou – the famous huimo sticks – in Hunan were also celebrated (Figures 17,18,19).
The ink sticks are rubbed gently with water against a concave stone to dissolve the ink powder; even today, the Chinese use stone slabs with a hollow to contain the necessary water. Most of these stones are the size of a hand, but there are also bigger ones; almost all are decorated along the edge and some are true works of art. Porcelain ink slabs also exist: they are often sold in wooden cases and are very highly prized.

The most costly ink slabs are those from Duanxi (around 100 kilometers from Canton) where the Mount Fuke quarries, on the banks of the Duanxi, have been worked for 1300 years.

In "Art et Sagesse en Chine", the renowned sinologist Nicole Vandier-Nicolas (1908-1987), expressed all of the astounding vivacity and virtuosity of China's artists of the brush; as the general Wang Xizhi (303-361 AD), known as the Sage of Calligraphy, declared in his work Preface to the Poems Composed at the Orchid Pavilion:
"Paper is the battlefield, brush is the sword, ink is the coat of mail, the ink stone is the moat that surrounds the stronghold, intuition is the general and skill is his adjutant ".
Legend has it that Wang Xizhi learned the deft wrist motions required for Chinese calligraphy through lengthy observations of how wild geese move their necks.
In the sixth century AD, the invention of block printing – printing using carved wooden blocks – gave a considerable impetus to ink-making. Highly regarded throughout the Far East, block printing is still practiced there today, along with all of the writing arts.

1.2 The spread of ink in the ancient world

It was not difficult to find black or colored mixtures for writing, even in countries like Arabia or Egypt, were fabric dyeing techniques were fairly well developed.
In these areas as elsewhere, ink was for centuries a simple mixture of powdered charcoal or lampblack and water, sometimes adding vegetable gum (gum arabic), gelatin and animal glues to create a suitable fluid vehicle for the ink.

Writings on Egyptian papyrus, the oldest evidence of which dates back to 2400 BC, indicate that a black liquid was used which, at least in the most primitive period, was prepared with lampblack and vegetable oil. Later, it would seem that ink was produced with lampblack held in suspension in an aqueous solution of gum arabic, used as a thickener to give body and the correct degree of viscosity to the ink (Figures 20, 21, 22, 23).

Some inks were extremely long-lasting, as demonstrated by the fact that ancient papyri from Egypt and Herculaneum are still perfectly legible today. Others were quite impermanent, and indeed could be removed simply by using a wet sponge: sponging and obliterating were synonymous. In these inks, the lampblack was insufficiently densened, and gum arabic, which also serves to bind the pigment to the substrate, was not used .

From Egypt, this type of ink passed to Greece and to Rome (as described in Dioscorides, III, 36). Of ancient Greek ink-making, we know very little: nothing but a phrase of Demosthenes that would seem to indicate that colored pigments produced by rubbing from some solid substance were used (τὸ μέλαν τρίβειν, Dem. de Cor. p. 313).

The Romans used and made ink, which took its name in Latin from its color: ater meaning black. A distinction was made between writing ink, atramentum scriptorium or librarium (Hor. Ep. ii. 1. 236; Petron. 102; Cic. ad Qu. Fr. II. 15.), and atramentum pictorium or tectorium, used by painters, apparently as a sort of varnish (Figures 24, 25, 26,27,28, 29,30).

In addition to black ink, the Romans also had red *atramentum rubrum* or *rubramentum,* and green *atramentum viride* or *viridamentum*.
Yet another type, *atramentum sutorium*, was used by shoemakers for dyeing leather; this product contained toxic substances, and indeed could be used as a poison (Cicero *ad Fam.* IX. 21.).
The red ink, produced by grinding cinnabar (mercury sulfide or native vermilion) or minium (red lead, or lead tetroxide) was used for the titles and beginnings of books and laws; *rubrum* is also the origin of the term rubric, from *rubrica*, or the red ochre in the inks used for the headings of laws.
The inkstand, or *atramentarium*, came in a variety of shapes, but was commonly cylindrical: it is believed that the most widespread type was that shown in a painting found in Pompeii, consisting of two cylinders joined together, each with its own cover.
To write on papyrus or parchment, the Romans usually used the *calamus*, a flexible reed sharpened and cleft at the point using a *scalptrum*, or penknife; as those who did not have the patience to sharpen a blunt calumus would simply change it, several (*fasces calamorum*; Martial, XIV, 38) were often kept near at hand while writing, stored in a case called a *theca libraria*. The best reeds for pen-making came from Egypt or from Cnidus.

The scribe at work was well described by Persius (Aulus Persius Flaccus, 34-62 BC), a Roman poet of Etruscan origin:

Persius,III, 10

"Iam liber et positis bicolor	*"Now we take up our book, and the two-*
membrana capillis inque manus	*colored parchment, well cleansed of hair,*
chartae nodosaque venit harundo."	*some sheets too, and the knotty reed"*.

The ancients also had metal pens, with the tip cut into a cleft nib. A fair number of these pens (which were made of bronze) have been found at archeological sites, but we know that they were a rare exception among the writing implements of the time.

On parchment or papyrus, the ancients thus wrote in ink using the red pen, whose tip was split like a modern nib to make it more flexible and to ensure that the ink would flow more freely from the pen. The tip was thin and pointed if it was intended for flowing cursive scripts, or broad if used for formal book scripts with a strong contrast between thin and thick strokes. This contrast depended on how the pen was held, or in other words whether the pen point was at an oblique angle, parallel to the surface, or horizontal.

The *calamus* was later joined by the quill (*penna*), generally those of the goose; like the reed pen, the quill was also pointed and slit to make the tip more flexible.

The two instruments – reed pen and quill pen – were in simultaneous use down to the end of the Middle Ages and beyond; the term *calamus,* in more recent sources, also designates the quill pen.

As a substrate, the ancients sometimes used wooden tablets similar to the wax coated types (on which letters were traced with the stilo, or stylus), but thinner and smoother, and thus suitable for writing with pen and ink. Called *chartae*, these tablets measured around 18 by 9 centimeters, and were usually not more than 1.5 mm thick. They were cut from the trunks of young trees, and were then dried and treated so that the ink would not spread.

Cicero, *Ad Qu.Jr.* II 14,1

"Calamo et atramento temperato, charta etiam dentata res agetur. Scribis enim te meas litteras superiore vix legere potuisse."	*"Well, this time I'll use a good pen, well-mixed ink and superfine tablets, for you say you could hardly read my previous letter."*

Crassus had his banners marked with letters of purple ink (*Dion Cassius. XL.18*); the political and commercial inscriptions on the walls of Pompeii were written in red, while in a later period, Suetonius says that a part of the poems which Nero recited at Rome (*Ner. 10*) were written in gold or gilt letters (*aureis litteris*) and consecrated to Jupiter Capitolinus.

Caked ink on the pen point was a source of irritation, as it is today; Persius *(Sat. III.14)* represents a foppish writer sitting down to compose, but the ideas will not flow freely…because neither will the ink! But he's afraid that adding water to dilute the ink will make things even worse.

Persius, *Sat.* III, 14

"…nigra sed infusa vanescit sepia lympha: dilutas querimur geminet quod fistula guttas."	*"…thinned now with water, the black fades, and we complain that the pen spits double dots upon the page…"*

In the Imperial period, poets whose work was not appreciated were commonly told:

"Wipe it all away with the sponge, tedious man, and leave the Muses in peace ";

Caligula (Suetonius, De vita caesarum, Cal, I. 20) even forced poets who did not meet his favor to erase their work by licking away the ink:

"scripta sua spongea linguave delere iussos..."	*"...ordered to erase their writings with a sponge or their tongue..."*

To produce an ink, the black pigments are, as we described earlier, "dispersed" in *binders* or *vehicles*. These substances, which thickened the aqueous mixture, differed according to geographical area and period: glue from horns and hooves, fish glue, egg whites, honey, gum arabic, linseed oil heated to varying degrees of thickness. Perfumes were often added to hide the objectionable odors of the organic ingredients. Ink was sometimes sold in the form of glutinous cakes which were dissolved, or "tempered", as it was called (hence the name of the dry *tempera* paints still used today) in water just before use.

Hebrew scripture mentions a substance called *deyo*, also cited in the Book of Jeremiah (XXXVI, 18: "*Then Baruch answered, He pronounced all these words unto me with his mouth, and I wrote them with "ink" – deyo – in the book*"), which may well have been a writing material similar to ink. According to Bernheimer, it was a black liquid, but differed from another, better known, black liquid for which the Greek term *kalkantos* was used*. Deyo* may have been a mixture of lampblack and resins which was then dried, as described in later reviews of Hebrew texts (Figure 31). It was diluted in water when the time came to use it. Later, honey and even nut gall were added to the mixture.

Other recipes for writing materials were also known. We have mentioned, for instance, inks containing cinnabar (mercury sulfide), minium (red lead, or lead tetroxide) and other mineral coloring agents, which are difficult to hold in solution in the vehicle, as they are very heavy and thus prone to *precipitation*.
Ink consisting of lampblack, water and gum arabic was in general use for writing on

papyrus, as Vitruvius and Pliny both testify. This has been confirmed by chemical analysis of the inks on the papyri found at Herculaneum.
According to Pliny, atramentum was made in various ways: chiefly with mixtures of soot, burnt resin or pitch, in furnaces which did not allow the air to escape (*Plin. II. N. XXXVI. 5. s. 25.*). Others made a kind of ink by boiling and straining the lees of wine, according to the statements of Vitruvius (*Vitruvius VII. 10*). The black matter secreted by the cuttlefish – sepia – was also used as atramentum (Cic. *de Nat. Deor.* II. 50 ; Persius, *Sat.* III. 12,13 ; Ausonius, IV. 76.). Pliny also observes that an infusion of wormwood with ink preserves a manuscript from mice.

2. Documentation of ancient inks

As Pliny the Elder (Caius Plinius Secundus, 23-79 AD) tells us, the Romans were familiar with an embryonic form of iron gall ink: in a solution of green vitriol (ferrous sulfate, an iron salt), they poured a decoction of *oak galls* (an excrescence on oaks caused by insects) together with pomegranate rinds, obtaining a black pigment that could be used for writing. This would appear to be the *atramentum sutorium* we mentioned above.

Philo of Byzantium (280 BC-220 BC) refers to an invisible ink (also called *sympathetic* ink) consisting of extracts of galls that was used for writing; it remained invisible until green vitriol was applied to the sheet. The writing then turned black, and could be read. Pliny writes of the *tithymalum* – a kind of spurge called at the time *herba lactaria* (milk plant) or *lactuca caprina* (goat lettuce) – which, he said, could be used as an invisible ink that worked in a different way: letters written with the milky sap of this plant would not be visible until dry and powdered with ashes.

Ovid (Publius Ovidius Naso (43 BC - 18 AD), in his *Ars Amatoria* or *The Art of Love* (*Ars. Am.* III.627) recommends writing with milk, unreadable until sprinkled with coal dust, which would stick to the slightly fatty surface left by the milk.

Ovid, Ars. Am. III 627-28

"…Tuta quoque est fallique oculos e lacte recenti Littera: carbonis pulvere tange; leges…"	*"…writ in fresh milk, all's safe and the eye deceived; dust it with coal, and you will read…"*

The Christian Latin poet Ausonius (Decimus Magnus Ausonius (ca. 310–395) gives the same advice (*Epist.* XXIII.21).

Inks of other colors used in antiquity included the *sacrum encaustum,* made with the purple pigment extracted from the hypobranchial glands of marine mollusks of the genus *murex,* added to water.
The pigment which produced this purple color was made by drying two species of the Murex snail (*Murex trunculus* and *Murex brandaris*) found in Mediterranean waters. One of the two species yielded a turquoise blue secretion; the other, a light red secretion. These dyes were mixed to produce a variety of colors, all highly prized. The snails were ground and left to dry in the sun for three days, and then boiled for ten days in lead pots. As around 12,000 snails were needed to extract a few grams of pigment, purple was enormously expensive (Figures 32, 33, 34, 35).
The first to use this method to produce purple pigment were the Phoenicians, who used it to dye cloth. For the Romans, purple was a symbol of power: the emperor wore a purple tunic, and senators were allowed to wear a tunic with a broad purple stripe.
Purple-red inks could be used only by the emperor to write his signature, and were forbidden to common mortals except for the emperor's sons and near relations to whom privilege was expressly granted.
In the Middle Ages, the use of *sacrum encaustum* was restricted to reigning monarchs. The gospels were written on purple parchment, in gold and silver inks, made by mixing fine metal powders in wine (which acted as a mordant) together with gum arabic or albumen.
Parchment was dyed purple, blue or even black. Many of the gospels copies between the fifth and seventh centuries are written on a purple ground whose various methods of preparation are described in medieval codexes: the *Miscellany codex 87* in the Chapter Archives of Vercelli, the *Codex 490* in the Chapter Library of Lucca, and the fifth century *Codex Purpureus Rossanensis*, or Rossano Gospels, now in the cathedral of Rossano Calabro.

Use was also made of the so-called *blue of Alessandria*, i.e., powdered copper treated with sand and saltpeter, which yields light blue copper nitrate; over time, this pigment tended to turn green as carbon dioxide in the air converted the copper nitrate to copper carbonate, or artificial malachite.

A substitute for gold was *auripigmentum*, consisting of yellow arsenic trisulfide (As_2S_3, the mineral *orpiment),* which is not poisonous because it is insoluble; it could also contain sandarac, or golden arsenic disulfide (As_2S_2, now called *realgar*), which becomes *orpiment* when heated.

Nor must we forget the treatise by Heraclius or Eraclius, *De coloribus et artibus romanorum,* an important source for the history of dyes, pigments and the "technical" arts in general. The work is divided into three books: the first two in verse, and the third and longest in prose.

The second section is entitled "*On the use of the fresh juices of plants in miniature painting*", and provides detailed descriptions of how to prepare pigments and dyes for manuscript illuminations and colored inks.

The oldest treatises on colors, pigments and paints written in the late Roman period are difficult to place precisely in the historical framework, as few sources that have survived; the emperor Diocletian, in fact, ordered the destruction of an enormous number of alchemical works and the like, for fear that someone would be able to transform base materials into gold.

Later medieval transcriptions of such recipe books (which have often come down to us incomplete) probably enjoyed a rather limited circulation, both because they were written in Latin (of varying quality), a language that was not widely used among artists (think, for example, of Leonardo da Vinci, who called himself, regretfully, "*homo sanza lettere*" – an unlettered man – because he knew no Latin), and because the few copies that were made were conserved in monasteries to which relatively few people had access. In addition, each copyist could introduce whatever variations the patron of the moment might happen to want, thus breeding errors and misreadings that were passed on without question.

Many colors of ink were used during the Middle Ages (as in the ninth-century *codex Vatic. Reg. lat. 129*): red, blue, yellow, gold, silver, green, white. Many curious recipes for preparing these inks can be found, and are interesting to record here.
Some of the oldest of these recipes to have survived are the formulas contained in the *Schedula diversarum artium* by the monk Theophilus Presbyter (XI-XII century). To prepare *encaustum,* he prescribes a dried and powdered extract of the bark of certain plants mixed with *green vitriol* (copperas, or ferrous sulfate), or a mixture of powdered iron and tannin. He also recommends that gold, silver and copper inks be prepared by pouring the powdered metal into decoctions of oak apples, vinegar, wine, or gum arabic in water. Theophilus also knows of a "Spanish black" used for a species of lacquer similar to Chinese ink; for red, he uses *minium* (lead tetroxide, or red lead) and *carmine* (cinnabar, mercury sulfide), while his white is *ceruse* (lead carbonate, or white lead). These substances, dissolved in egg whites, vegetable gums (*tragacanth,* other *gummy saps*, etc., serving as binders and dispersants), in wine or vinegar, or in plant juices (acting as mordants, and improving adhesion), were also part of the formulations used in miniature painting.
The *Miscellany codex 87* in the Chapter Archives of Vercelli and the *Codex 490* of Lucca contain similar formulas for the so-called *chrysography,* or writing in gold.

A fifteenth century manuscript entitled *“Segreti per colori”* – Secrets of Colors – now housed in the library of the University of Bologna provides us an idea of the state of protochemistry in the Italy of that day. The work is divided into eight chapters; it discusses blue, and lapis lazuli or ultramarine blue in particular, and the various ways of producing it. In the third chapter, after describing how to make blues with the juices of several plants, it turns to a number of dyes, including indigo dye and the methods for producing it from *woad*. The fourth chapter teaches a number of ways of preparing verdigris or copper green, the most singular of which recommends that the color-maker “… *place copper sheets in vessels under manure, then after one or two months, treat the product with the strongest vinegar and cover the vessels with manure once again. After two months more, the copper green* (basic copper acetate) *is ready”*.
Chemically, what happens here is that the copper reacts slowly with the acetic acid in the vinegar: this produces a greenish salt, while the hydrogen sulfide fumes – aka sewer gas – arising in the manure heap can accelerate the process.

In the Middle Ages, ink making was largely the work of *monks*, who for centuries made up the ranks of the scribes to whom history owes its undying gratitude for the recovery and preservation of much of Western classical culture and the chronicles of its events. Take, for example the long parchment scroll, dating from the eleventh century, called the *Chronicon Novaliciense*, at the Abbey of Novalesa in Piedmont, founded by Charlemagne (who among his many other merits did much to promote writing), which narrates the life and doings of the abbey in the centuries that only those who do not know their history call the “Dark” Ages”.

In the monasteries, ink was prepared according to traditional formulas, which were often jealously guarded secrets. There were also specific rules for storing ink.

By the late Middle Ages, lampblack ink had begun to lose its importance; we hear of it only in the treatises of the painters and illuminators of the period, who used it in small quantities as a pigment in their paintings.
Lampblack ink has the valuable property of not being reactive, thanks to the fact the carbon used in it is chemically inert: it is not subject to chemical changes with the passage of time, and contains no substances that can damage the substrate to which it is applied. In addition, the carbon particles do not fade in light: in other words, they are *lightfast*. However, this type of ink has two serious drawbacks which doubtless limited its use: it tends to smudge in moist environments because it does not penetrate deeply into the substrate, and, consequently, it can be washed off, or even removed by rubbing or scraping, by anyone who intends to alter a piece of writing. This latter aspect may have led to the practice of adding small amounts of ferrous sulfate, which over time is subject to slow chemical reactions that transform it into a variety of iron oxides, leaving dark brown deposits. The highly soluble ferrous sulfate penetrates into the paper, leaving these deposits, which are not readily removed. As a result, the writing is very difficult to erase.
Washing a document written with this type of mixed (lampblack and ferrous sulfate) ink will only remove the carbon particles on the surface, while the ferrous sulfate deposits will remain. Even scraping will not be *fully* effective in removing the writing without damaging the surface of the sheet, given the iron salt’s deep penetration.
When larger and larger amounts of ferrous sulfate are added, however, the brown from the iron oxides overwhelms the black from the carbon particles.
This problem could be avoided only when the reaction between tannin (gallotannic acid) and iron salts had been understood. As adding galls (which contain this tannin) turned the ferrous liquid black, a mixture of carbon ink and iron gall ink would not change color over time.
This is one of the theories that have been advanced concerning the birth of iron gall inks, which were thus developed later than lampblack-based carbon inks. Their use began to spread in the Middle Ages, though there is no lack of earlier mentions.

3. Iron gall inks

The chemical reaction between tannin and iron salts (*ferrous* salts, i.e., at a lower oxidation state than ferric iron) has been known since antiquity. The oldest extant Greek mentions of it are found in the Leyden Papyrus and in the Stockholm Papyrus. Pliny the Elder describes an experiment in which he wet a papyrus that had been soaked in an infusion of tannin with a solution of iron salts: the papyrus immediately turned black.

Several hundred years later, Martianus Minneus Felix Capella (fifth century), a native of the Roman province of Africa who appears to have practiced as a jurist in Carthage and became a writer late in life, composed a sort of encyclopedia that achieved canonical status during the Christian Middle Ages, *De nuptiis Mercurii et Philologiae* ("The Marriage of Mercury and Philology"), in which he supplies a formula for preparing an ink that he calls "*gallarum gummeosque commixtio*". This ink was produced by mixing varying proportions of an infusion of *galls*, tannin-rich growths which develop on certain trees (oaks, for instance) when insects deposit their eggs in the plant tissue, green vitriol (ferrous sulfate) and *gum arabic* (the latter being used as a binder to hold the pigment in suspension). The formula that Albertus Magnus gives in his *De rebus metallicis* is of the same kind.

Iron gall ink was widely used in the Middle Ages, though the first known recipe is contained in the treatise by Theophilus Presbyter we mentioned above. In the West, its use was virtually universal, and many variations can be found from the fifteenth century onwards. Iron gall ink was employed in writing an enormous number of documents, as well in printing woodcuts.

This ink's color is due to its main component, ferrous gallate, which forms when a generic tannin reacts with a ferrous salt. The reaction takes place with precise quantities of tannins and metallic salts (*molar ratio* of 4 to 1); all of the iron combines with the tannin, forming a complex with it that produces a chemically stable ink where the ferrous gallate acts as a pigment. Under these conditions, however, the reaction proceeds fairly slowly, and it thus takes time to reach completion. The ink would behave as a coloring agent, becoming indelible, only if it was used immediately after it was prepared. With the proportions we have indicated, moreover, it took a few seconds of exposure to the air for the iron in the compound to oxidize completely and turn black. For this reason, there was a tendency to add an excess of metallic salt beyond that required to combine with the tannin: though this ensured that the ink would turn black immediately, it also made the compound unstable. It should also be borne in mind that while the ink would stay black for a considerable length of time, once all of the excess iron had oxidized, it would turn brown, and this is thus the color we find on most antique manuscripts. Not only does the excess ferrous iron turn the ink brown as it oxidizes, the oxides then tend to crystallize, forming hematite (ferric oxide) microcrystals that appear as iridescent flakes. These reactions, together with the acid properties of iron gall ink, can damage the cellulose in the paper to the extent that the ink may even burn holes through the areas where writing was applied.

The public and private documents written in "tanno-gallate of iron" preserved in the world's archives and libraries testify to the widespread medieval use of iron gall inks, which became even more common from the twelfth century onwards. These inks were usually low in grade and of poor quality: a muddy fluid, easily precipitated, which deteriorated quickly. A length period of experimentation was needed to modify or overcome its defects, as well as to gain information about the different tannins, the proportions of each constituent, and the correct methods of preparation. From the recipes that have been found, we can say that the raw materials and methods used varied widely, with those that were chosen depending on geographical area, personal convictions and the materials at hand (Figures 36,37,38,39,40).

Tannins vary in composition; some are polyphenols of moderately complex structure; others also contain esters of glucose or other sugars. When exposed to light, the color of tannin becomes more intense. They are water-soluble compounds: tannin is usually extracted from infusions with water or water and ethanol. As the latter evaporate at low temperature, the tannin is precipitated from solution.

A recipe contained in a codex dating from 1412 and published by Ebert *(Zur Handscriftenlkunde,* Leipzig, 1825, page 35) recommends mixing powdered nut gall with water or beer and then subjecting the mixture to the reaction of green vitriol (ferrous sulfate). This basic formula remained almost unchanged in later centuries, and was often applied empirically, i.e., without any rational or uniform way of establishing the proportions of each ingredient. The *Liber illuministarum pro fundamentis auri et coloribus ac consimilibus,* written sometime in the 1500s at Tegernsee, near Munich, and now in that city's Staatsbibliothek), contains a recipe for ink which it summarizes in a Latin distich, or couplet:

Integra sit galle, media sit uncia gummi
vitrioli quarta. Apponas octo falerni.

Thus, the recipe calls for*:* nut gall (one full ounce), gum arabic (extracted from several species of acacia and soluble in water, half an ounce); iron vitriol (one quarter of an ounce), and eight ounces of Falernian wine, celebrated since the time of the ancient Romans.
In the sixteenth century, the composition of iron gall inks achieved a certain uniformity all over Europe, thanks to the standardizing influence of the Florentine inks then in widespread use. Throughout the fourteenth, fifteenth and sixteenth centuries, in fact, Florence led the rest of Europe in ink making, producing more and better inks than anywhere else.

In the 1500s, after the advent of printing with movable type and the more extensive use of the vernacular rather than Latin, "books of secrets", or collections of recipes and practical techniques of all kinds, began to enjoy wide popularity. An interesting theory holds that this was due to the need to use manpower that did not have the skills that the lengthy apprenticeships required by the hidebound old system of guilds had ensured: when the mercantile middle classes took the reins of trade in the sixteenth century, the new workers had no longer received years of training under a master. Hence the need for handbooks that could explain what once had been the secrets of each craft.

The first examples of these new compilations of recipes in the vernacular appeared in Germany, but some of the most famous were published in Italy, including "*I segreti del reverendo Alessio Piemontese*" attributed to Girolamo Ruscelli (Viterbo 1504 - Venice 1566), which went through 104 editions in at least seven languages (Italian, Latin, English, French, German, Spanish and Flemish) in the space of little over a century. Ruscelli's authorship is certain, as the title page of a Venetian edition of 1567 reads "*Secreti nuovi di maravigliosa virtù del signor Ieronimo Ruscelli i quali continovando a quelli di donno Alessio, cognome finto del detto Ruscelli, contengono cose di rara esperienza, & di gran giovamento*" (New secrets of marvelous worth by Master Ieronimo Ruscelli, which continuing after those of Father Alessio, assumed name of said Ruscelli, contain things of rare experience and advantage). The treatise was enormously successful, as witnessed by its many printings and by the fact that it provided the material for many recipe books published in the course of the seventeenth and eighteenth centuries.

An eighteenth century edition dated 1783 and printed in Venice by Francesco Locatelli under the title *“Secreti del reverendo D. Alessio Piemontese, divisi in quattro parti. Nuovamente ristampati e da molti errori ricorretti*” (Secrets of the Reverend Father Alessio Piemontese, divided into four parts. Newly reprinted and purged of many errors) describes a number of curious uses for pigments and dyes. For example:

- To dye a white dove gold: “*Take saffron, well ground and pounded, and mix it with bile from the Luce, and with this color the bird”.* Saffron is expensive, but less than gold, which it resembles in color, while the bile of many fish (the pike, in this case) does in fact have an adhesive effect and, once dry, leaves a shiny surface.

- To make black dye to color a horse: “*Take pounded gall, and make distilled water of it, and with this dye a white or sorrel horse, and it will become black; and to give a black horse a white blaze, take the droppings of chickens, place them on the face of the animal for a day, binding them well, and then remove them, and where the droppings were, there it will be white.*” The tannins from the gall dye the horse’s coat, but the effect of chicken droppings is something that the chemist is hard pressed to explain – much less believe.

Other authors such as Leonardo Fioravanti and Domenico Auda were also widely read, and were still copied as late as the nineteenth century, but the recipes they offer were far less “innovative”.

Any one of the recipes in these books of secrets, that provided by Pietro Maria Canepario in his 1619 treatise "*De Atramentis cuiuscumque generis*", for instance, can be taken as an emblematic example of the seventeenth century method of preparing iron gall inks:

"*For four days, mix four pound weights of white wine, a cup of the strongest vinegar and two ounces of crushed gall. These then are cooked over the fire until a quarter has evaporated. Then strain the liquor and afterwards add chips of gum arabic, two ounces, mixing well and returning to the fire so that it boils for as long as it takes to say three paternosters. Take it then from the fire and add three ounces of ground Roman vitriol, stirring the while with a stick until it is almost cold. Then pour it into a glass cup, kept well away from the light and air. After it has stood in good weather for three whole days, it can be strained and used.*"

As can be seen, the main ingredients were always the same: a tannic substance of some kind, iron salts, solvent, and a binder-emulsifier such as gum arabic.
The method of preparation consisted of extracting the tannic and gallic acid from the galls, which for this purpose were crushed and left to steep in the solvent (water or wine) for a week, and then boiled. At times, the galls were boiled without steeping them first in solvent. Boiling continued until two thirds of the solution had evaporated, reducing it to one third of its original volume. The iron salt was then added, and reacted with the tannic and gallic acids. The emulsifier was added at this point (though it was sometimes added before the iron salt) to hold the black particles that formed through the chemical reaction in suspension. Other additives to increase fluidity, prevent fermentation, or scent the ink could be used as needed, as we mentioned earlier.

The inks produced in this way, however, were excessively acid. The reaction that forms ferrous gallate also frees sulfuric acid from the ferrous sulfate, which remains in solution and, over time, will corrode the substrate to which it is applied, paper in particular, and may even eat holes right through it. This excessive acidity is characteristic of the writings preserved in Italy’s archives, which have an urgent need for costly and time-consuming restoration as a result.
This acidity was compounded through the use of vinegar, added for its acetic acid

content, and of wine, added for its ethyl alcohol content, both of which served to improve the solubility of the ferrous gallate pigment and help it penetrate in the paper, mordanting it into the fiber.

Articolo VII. During the sixteenth century, a number of writers give details of the better-known methods and procedures. The celebrated mathematician and mechanical experimenter Girolamo Cardano (Pavia 1501 – Rome 1576) in his *De subtilitate, libri XXI (Basileae per Lvdovicvm Lvcivm, Anno 1554*), and *De Rerum variegate, libri XVII (Basileae 1581, per Sebastianum Henricpetri*), suggests recipes and different types of black and colored ink, demonstrating that Renaissance scientists had to do a bit of everything to make ends meet.
Articolo VIII.
Articolo IX. Alessio Piemontese, whom we have already introduced as the pseudonymous author of *De secretis libri septem (*1557) give recipes for black (decoction of gall, white wine, copperas and gum arabic), for other colors (made with Brazil wood, tin oxide, purpurin and stannic sulfide), as well as for gold and silver paints made from the powdered metals or using stannic sulfides and mercuric sulfide as pigments.
These were often highly toxic mixtures, to which even more potent poisons could be added (deadly salts and soluble oxides of arsenic, for example, or gut-wrenching antimony) for all manner of unnamable purposes and foul ends, as portrayed with massive doses of suspense in recent bestsellers and various efforts at fictionalized history.
An erudite and highly philosophical work on colors and their historical and social importance was penned by the humanist and poet Antonio Telesio (1482 – 1534), who latinized his name as Antonius Thylesius (Antonii Thylesii Cosentini *Libellus de Coloribus, ubi multa leguntur praeter aliorum opinionem);* the learned author, however, has nothing of technological relevance to offer, limiting himself to discussing the improbable influences of colors on human destiny.

Giovan Battista della Porta, polymath of markedly esoteric interests *(Magiae naturalis libri viginti,* 1567), resuscitates Pliny the Elder's recipe for sympathetic ink, recommending a decoction of gall nuts for making letters reappear that had been written in Roman vitriol (ferrous sulfate), practically invisible on paper until brushed with the gall solution that causes the black iron salts to form. Other types of sympathetic ink mentioned by della Porta include certain plant juices that become visible when exposed to heat (because of the formation of tarry substances occurring as a result of thermal *cracking*, i.e., the partial combustion or degradation of thermally unstable molecules); a clear liquid that turns white when the paper is heated and charred (probably as a result of the dehydration of a salt which is colorless in the hydrated state), or black if black powder is sprinkled on it (because the powder, which presumably contains a little glue, gelatin or gum arabic, sticks to the letters).

An indelible ink made with oil and lampblack is mentioned by Johann Jacob Wecker *(De secretis,* Basle, 1582), quite a believable formula, since lampblack is well known to be impossible to remove if well anchored to the substrate, which can be achieved through the use of animal glue or even isinglass, added in small quantities to the mixture so as not to detract from the ink's fluidity.

Several recipes for inks based on gallotannic acid are found in Hebrew texts from the sixteenth century: one, for example, calls for one ounce of gum arabic dissolved in white wine and two ounces of copperas, to which three ounces of gall in thirty of white wine were added. The copperas solution was boiled, and the gall solution poured into it, to produce the black pigment. As wine, however, was prohibited by rabbinical law and Hebrew tradition, the authors who reported this formula must have found that it had little to recommend it.

The main characteristics of iron gall inks continued to vary widely for many years, until, in 1626, the French government concluded an arrangement with ink makers to standardize production and thus guarantee quality. Other governments later followed suit with similar agreements.
After this, improvements to traditional formulas proliferated, from those by Otto Tachenius *(Hippocrates Chimicus,* 1666), to the work of the famous chemist Robert Boyle (originator of Boyle's Law of the behavior of gases), who attempted to explain the reactions that take place when copperas is added to infusions of gall in *Some considerations touching the usefulness of experimental Natural Philosophy* (Oxford, 1763).

Here, I would like to record a typical eighteenth century formula for writing ink hailing from my own home region of Piedmont, which I found in a manuscript by an otherwise unknown priest, one Father Brocero of Savigliano, near Torino; it calls for:

Roman gall, three ounces,
Rock alum [hydrated aluminum sulfate] one half ounce; gum arabic, one ounce;
Copperas [hydrated ferrous sulfate], two ounces.

These materials are crushed, placed in one *brenta* (50 liters) of rainwater (essentially, distilled water) and left for eighteen days in the sun: an ecological way of evaporating the excess liquid. A little spirit (ethyl alcohol) is added, and the whole is filtered. The alum, or aluminum sulfate, is used as a mordant to anchor the ink to the cellulose fibers in the paper.

Articolo X. To conclude our discussion of iron gall inks, then, we can say that from the sixteenth century onwards, there was a certain uniformity in the composition of writing inks throughout Europe, thanks to the standardizing efforts of monks, craftsmen, merchants, alchemists and governments. In their celebrated (1751-1772) Encyclopédie ou Dictionnaire raisonné des sciences, des arts et des métiers, Diderot and D'Alambert illustrate the art of writing with the classic goose quill, still used for special documents and appreciated by purists of calligraphy today (Figures 21, 22, 23, 24).

Iron gall ink's relative indelibility also ensured that it was also universally used as "safety ink", as it is in fact difficult to remove completely from the substrate, even by scraping. The discovery of the bleaching power of chlorine in the eighteenth century made it possible to erase iron gall inks, though only temporarily: bleached, the ink loses its color, but after some time, the oxygen in the air re-oxidizes the iron, and the writing reappears, much faded but still legible.

To prevent chlorine from having this effect, the Swiss maker Leonhardi developed a formula for a safety ink that combined the properties of iron gall ink with those of active dyes in an acid solution, which would not lose their color when oxidized by chlorine.
Iron gall ink began to fall into disuse in the early twentieth century after the introduction of pigment-based India inks, which did not damage steel pens (readily corroded by the sulfuric acid in iron gall ink), and disappeared entirely with the invention of the ballpoint pen, which use an oil-based ink similar to printing inks.

In 1990, Russian scientists discovered the composition of a very old (probably seventeenth century) and highly prized Tibetan writing ink, known as the "Ink of the Seven Gems", used in the sacred manuscripts of the Buddhist monks of that country, then (in the 1600s) virtually unexplored. Using modern analytical methods, it was determined that this ink contained gold, silver, copper, coral, lazurite (a component of lapis lazuli), malachite and mother of pearl. Not exactly economical, but its iridescence on shellacked paper is almost incredible.

4. Printing inks

Letterpress printing (Figures 41,42,43,44,45,46,47,48,49), or in other words, printing text with movable type, probably arose in Germany through the work of Johannes Gensfleisch, known as Gutenberg, and his followers around 1440.
The inks we have described so far, whether iron gall-based or aqueous solutions of gum arabic containing lampblack pigments in solution, cannot be applied uniformly to metal type, as they are too fluid and thus tend to smear or run, rather than spreading evenly so that they transfer cleanly and legibly to the paper.

Gutenberg thus had to use oils, which adhere more effectively to metal type. It is thought that, initially, oils were added to iron gall ink, but there is no evidence to support this conjecture.

Very little historical evidence of any kind, in fact, is available concerning the first printing inks. Nevertheless, it should be emphasized that the ink in the celebrated 42-line Bible (1450-52) is essentially perfect, undoubtedly the result of lengthy research which links Gutenberg to the Flemish masters who pioneered the use of oil paints (with linseed oil) in the fifteenth century. Thus, the first printed works employ dense black inks that are free from the brownish overtones that are still to be seen in many works dating from later centuries.

In his *De inventoribus rerum*, Polydore Vergil maintains that printing ink was invented by Schoeffer, but it is certain that Gutenberg himself formulated his own ink: he could not have printed the first Bible so perfectly without a good ink, whose formula was thus not something that could simply be extemporized.
Another, less reliable tradition would have it that printing with movable type was invented around 1440 in the Netherlands by Laurens Janszoon Coster of Haarlem, who could easily have had contacts with the world of Flemish painting.

In general, early printing inks consist essentially of two components: a black or colored solid pigment, and a viscous or pasty fluid called *varnish* which acts as a vehicle and binder for the pigment so that it can be used to ink metal type.
The pigment must be perfectly ground, or in other words reduced to extremely fine powder and mixed uniformly in the varnish.
The resulting mixture, dense to the point of stickiness, was spread onto the type, originally with a gloved hand, and later using *ink balls* made of leather stuffed with wool or hair and attached to a wooded handle.
In the first printed books, or incunabula, the chapter initials were hand-colored – or rubricated – with the usual tempera paints. Soon, however, red and blue inks came into use, made by mixing the linseed oil with cinnabar (for reds) and lapis ultramarine or azurite (native copper carbonate) for blues.

A document dating from the late fifteenth century in the *Diario della Stamperia di Ripoli* lists the materials purchased by a printshop run by the nuns of the Florentine convent of Ripoli. Consequently, we know that the convent bought linseed oil, turpentine, resin and linseed varnish, solid or liquid according to the season, as the temperature has an enormous influence on printing ink: the hotter the weather, the more viscous the ink must be.
Turpentine (made by distilling the wood and sap of conifers) was heated until all of the volatile content had evaporated, leaving *rosin*, a solid resin also known as Greek pitch or colophony – from Colophon in Lydia – which gives body to the ink so that it does not spread on the page or leave black spots or halos around the printed lines; using too much resin, however, will produce an excessively tacky ink that can cause the paper to dry and tear prematurely.

A typical recipe for early printing inks calls for three parts of lampblack, ground together with around 15 parts by weight of boiled linseed or walnut oil. Every morning, the pressmen would have to prepare the amount of ink they would need for the day, as both linseed and walnut oils are *drying oils* or *driers* that limit the amount of time that the ink remains at the right consistency for printing.

According to Stoyle, in his preface to C.H. Bloy's *A history of printing inks,* one of the major texts in this area, the lack of information about early inks is due to the printers' marked reluctance to disclose the secrets of their art. Each of the most celebrated printshops, in fact, guarded their knowledge with care, often obliging their workers to swear oaths of secrecy and threatening those who disclosed the master's formulas with dire punishments and terrifying reprisals.

This newfangled new business of printing is rather oddly illustrated in one of the plates in the *Novo teatro di machine et edificii : per uarie et sicure operationi; có le loro figure tagliate in rame é la dichiaratione e dimostratione di ciascuna; opera necesaria ad Architetti, et a quelli che di tale studio si dilettano*, (the New Theater of machines and buildings: for safe and divers operations; with their representations engraved in copper and the statement and demonstration of each; a work necessary for Architects and those who delight in this study) published by Vittorio Zonca of Padua in 1656 (Figure 28). More accurate, and of greater technical interest, obviously, are the plates in the first great encyclopedia, the *Encyclopédie ou Dictionnaire raisonné des sciences, des arts et des métiers*, published a century later by Diderot and d'Alambert between 1750 and 1770, which depict letterpress printing (Figure 29), the printing press and associated equipment**,** and the copperplate press.

4.1 Modern analyses of Gutenberg's ink

There is very little historical evidence concerning early printing inks. As no precise ink recipes have survived from printing's experimental days, we have no way of determining the chemical composition of the inks used to print the incunabula with absolute certainty. Recently (2003-2004), analyses based on the most modern techniques have been conducted on original sheets of the Bible printed by Gutenberg in 1452, the famous 42-line Bible, the first complete book printed using letterpress techniques.
The results of these investigations, carried out by Bruno Fabbiani and Alessandro Gusmano, who formerly taught at the Politecnico di Torino, using *IR and micro-Raman spectroscopy* (with equipment provided Prof. M. Carnasciali of the Università di Genova Department of Chemistry), indicates that the ink employed by Gutenberg in the 42-line Bible contains linseed oil, walnut oil and lampblack. Walnut oil yellows more quickly than linseed oil but, if heated, dries more quickly: a determining factor for the amount of output a printer can achieve. A full report of these studies was given at the conference entitled "*Printing from Mainz to Subiaco*" held in Subiaco in September 2006, and in the published Proceedings of this conference.

Earlier, in 1985, *Scientific American* published an article by two University of California researchers, Richard Schwab and Thomas Cahill, who subjected the 42-line Bible – the B42 – to a nondestructive analysis technique they called *Proton Milliprobe Analysis*, which involved bombarding sheets of the B42 with a proton beam and then using a spectrometer to analyze the fluorescence spectra of the X-rays emitted. Their findings indicated that the ink prepared by Gutenberg contained lead and copper, as was shown by the spectrometric results.

This method of analysis was based on bombing a sample of the B42 with a proton beam accelerated by a cyclotron. The collision between protons and metallic elements contained in the sample causes the emission of X-rays and electrons, thus allowing to

reveal the metals present in it through induced fluorescence, as metals are characterized by typical wavelength ranges. Copper and lead in the ink corresponded respectively to 55% and 36% of the total amount of calcium (to which a value of 100 was assigned) in the printed sample, with different values in different pages.
The actual percentage by weight of copper and lead salts falls far short of the amounts that are required as pigments in inks. The American research study, in fact, mentions lampblack as a pigment in the Gutenberg ink.
However, Cahill maintains that the variations in the copper/lead rate found in the pages of the B42 are due to the fact that Gutenberg's workers, while using the same recipes, were quite wanton in adding to the ink copper and lead salts, whose chemical and physical functions cannot be explained.
As a matter of fact, the catalytic function of heavy metals in the oxy-polymerization of drying oils, i.e. the increase of their drying speed by adding, for example, cobalt and manganese salts (soaps) is a much more recent finding; moreover, to perform this function copper and lead salts must be soluble in the ink vehicle, consequently the addition of salts with this purpose in years as early as 1450 looks unlikely.

4.2 Composition of Gutenberg's inks

The black copper and lead salts that were available in Gutenberg's day for use as pigments are lead sulfide (PbS, a crystalline material occurring naturally as galena) and copper sulfide (occurring as various hard, crystalline cuprites with varying sulfur content), which could be found as such in Germany's many mines.
It is not clear, however, why Gutenberg should have wanted to complicate his task by using costly substances that in their natural state occur as hard crystals, and thus require lengthy grinding in order to produce fine powders, which are not only very heavy but also yield a black that, though similar, is of lower quality than the economical and widely available lampblack and the black from oils.
Moreover, these metal powders' high density means that they will precipitate even in drying oils that, like linseed oil, have been partially "boiled", or in other words, heated to drive the water out of the oily extract of flax seeds and increase the oil's viscosity.
Using the metal salts found by the two American researchers as pigments would thus be both useless and dangerous. Two other possible explanations for their presence can be put forward:

- The traces of metal detected in the analysis were in fact present in the ink, but came from the metal type or other portions of the formes used by Gutenberg, and were "incorporated" onto the paper as a result of the pressure exerted during printing; or
- The traces of metal derive from burning coal containing these metals to make lampblack, which, as the IR and micro-Raman analyses demonstrate, constituted the pigment in Gutenberg's ink.

The fluorescence spectrometry method used by Schwab and Cahill, though excellent for detecting trace metals, cannot identify carbon (or other elements whose atomic weight is less than that of sodium). Consequently, lampblack, though a commonly used black pigment, can be neither detected nor measured by this technique.

The French historian Guy Bechtel, in his *Gutenberg et l'invention de l'imprimerie*, published by Librairie Arthème Fayard (1992), translated into Italian and published by SEI in 1995, takes up Schwab's analyses and presents them with additions of his own, doing so with glaring errors that reveal his ignorance of chemistry.

The analysis shows that the minimum quantities for the elements found on the bare paper of the B42 (sodium, silica, chlorine, potassium, calcium, manganese, iron) are present in identical quantities on the inked portions of the paper; here, however, sulfur, copper, lead and traces of titanium also appear, apparently from the ink.

It is very likely that these minerals – sulfur, copper, lead and titanium – were part of the composition of, and were thus contributed by, the coals in Gutenberg's area that were burnt to produce soot and lampblack, or for heating. Even in the not-too-distant past, the ashman would go from house to house collecting soot, and chimneysweeps would sell it to makers of ink and shoe polish.

On page 459 of the French edition, he states that "the color achieved is always the same despite the variations in the formula of the ink [by which he means differences in the relative proportions of the heavy metals found in the analysis] which occur from one page to the next".
Aside from the fact that these variations would have virtually no influence on the *optical density* of the printed ink (and here we have a demonstration that Bechtel believes these metals, and not the lampblack, to be the pigments), if the American investigators found variations in the ink mixture on different pages, but the color of the printing does not change, *it is obvious that this color does not depend on the metals*, but on something else. That something is the lampblack, whose "black intensity" (scientifically measurable as optical density) varies according to combustion conditions, purity and the fineness attained in the micro-grinding process. In addition (and this is a fundamental fact), lampblack is extremely light: as a result, it forms stable dispersion without precipitating in oily vehicles, which can thus be applied evenly to metal type surfaces.
On the same page of this volume, Bechtel states that "on certain days, significant variations in the percentage of copper versus lead can be seen [in the B42], a fact we find inexplicable". The fact, however, can be explained with no difficulty whosoever, because the composition of lampblack varies according to the type of coal that was burnt. This in turn affects the composition of the ink, which had to be prepared every day, or nearly every day, since it hardens rapidly if left in the open air because linseed oil and the other drying oils employed are readily oxidized and polymerized.

Consequently, the relative proportions of copper and lead would have varied if the daily batches of ink were prepared from lampblack made with coals from different areas, containing different percentages of these metals.
Conversely, if the lampblack is made with coal from the same source, the relative proportions of copper and lead will be the same in each batch of ink, regardless of the day it was prepared.
If, then, Bechtel is correct in saying that 294 production sequences with different batches of ink (i.e., having different proportions of copper and lead, proportions that Bechtel fails to specify) can be identified in the B42, this simply means that the different types of lampblack and soot at the printshop were mixed together, not that imprecise additions of metal salts to a pre-determined recipe were made.

Pure or purified metallic salts were, and still are, far more expensive than lampblack. In addition, it is improbable that sufficient quantities could have been obtained in a period when chemistry was still alchemy; therefore, they could not have been added.
The amount of lampblack needed to produce a good black is quite modest: around 3 to 5%, as lampblack is extremely light in weight.
The abovementioned metals are also found in Gutenberg's 36-line Bible, i.e. the B36, but not in the same quantities; this elements supports my theory, as in that case lampblack was obtained from other coals.

The Cahill team has used the same method to analyze the 36-line Bible and the fragment known as the *Sibyllenbuch* which is kept in the Gutenberg Museum; here, too, considerable quantities of copper and lead have been detected, which therefore has been regarded as "Gutenberg's signature"; my opinion, however, is that these are accidental facts, due to the composition of the fuels from which the lampblack was obtained.

Rather than by adding metal salts, the ink mixture's drying behavior could have been easily altered by adding small and variable amounts of walnut oil to the main linseed oil, as the two oils have different drying behaviors. As an alternative, it would be possible to adjust the linseed oil's viscosity to reflect the temperature, heating it for longer periods in hot weather and shorter periods in cold weather.

Unfortunately, the incursions of non-specialists, the rarity of Gutenberg's surviving output, the lack of cooperation shown (often for chauvinistic reasons) by museums and of serious scientific analyses with modern instruments which lasted, with very few exceptions, throughout the twentieth century have caused continued uncertainty about the genesis of the B42 and the invention of printing types.

5. Renaissance, seventeenth century and eighteenth century inks

Printing flourished in the sixteenth century. Thanks to the elegance of the typefaces available at the time, and the excellent paper – made from cotton rags – then in general use, the output of that century stands as a brilliant synthesis of artistry and technique.
In the seventeenth century, faced with growing demand for printed books in a Europe ravaged by war and pestilence, printers were forced to sacrifice quality to cope with the rising costs of raw materials. As a result, the editions of this period are often remarkable only for their poor ink and poor paper.
A seventeenth century Dutch method for preparing the varnishes used in printing inks, described by Joseph Moxon of London (1627-1700), celebrated experimenter and author of *Mechanick Exercises on the Whole Art of Printing*, called for a good linseed oil. After the oil was heated, an onion was dropped into it to gauge the oil's temperature on the basis of how quickly the onion cooked. *Rosin* (also known as Greek pitch), dried pine resin ground to powder in a mortar, was then added, and the oil was put back over the fire to dissolve the rosin and boil down the mixture to produce a homogenous varnish. At that point, one once of litharge (lead oxide) was added for every four gallons of ink to remove the tarry sludge that had formed in the mixture: the heavy oxide binds and precipitates the tarry residues. The mixture was then boiled again over a slow fire, allowed to cool, and filtered, after which it was set aside to rest as long as possible before adding the pigments needed to make ink.
According to a recipe by the French printer Martin-Dominique Fertel (1684-1752), on the other hand, walnut or linseed oil was boiled for two hours, adding bread crusts to remove the grease: in other words, the bread was used to absorb the tarry sludge and the excess oil that did not combine with the varnish.
Once charred, the bread crusts were removed and the oil was boiled over a slow fire for another three hours. Since a "weaker", i.e., less viscous, oil was needed in the winter because of the lower temperatures in the printshop (radiators, obviously, were far in the future), Fertel recommends adding an egg (an egg!) at the end. He also says that using turpentine, because of its rapid evaporation, prevents halos from forming around the printed letters, but that overusing it can make the ink dry too fast, causing the work to stick to the type, and thus tearing the paper when the print is pulled.
Consequently, turpentine was to be added to the oil only in a proportion of one to ten. Preparing the turpentine entailed another two hours of boiling, and the turpentine was added to the oil while they were both still hot; the mixture, then, was boiled for another quarter of an hour. Making a good product thus took a long time – and involved serious fire hazards!

Printing's fortunes revived in the eighteenth century, and ink factories sprang up just about everywhere, particularly in England, France and Germany, though all trace of these small ink-making operations has since been lost. The first in order of time, according to the authoritative *Annals of printing* by W. Turner Berry and H.E. Poole (London, 1966), was a company set up in King Street, London, by William Blackwell (a surname that, for an inkmaker, says it all), in 1754.
Other sources assign precedence elsewhere, but in the absence of reliable documentation, we must accept Blackwell as Europe's first ink factory.

The chemistry of the Age of Enlightenment came to the inkmakers' aid with a number of publications – the *Encyclopedie* by Diderot and d'Alambert first and foremost – that illustrated combustion, distillation, mixing and all of the other techniques required to produce pigments and vehicles in explanatory images.
Lampblack continued to be prepared as it had been for centuries, using that classic tool of ancient chemistry, the copper *retort* (which takes its name from its shape, *retorta* in Medieval Latin meaning "bent back") filled with oils, pitch, tar or coal. Heated, these materials would be broken down and distilled to produce carbon-rich fumes, which are

burned under a large metal hood on which the coarser lampblack is deposited. The finer carbons is carried by the rising air through a hole in the hood, ending in a cold chamber on whose walls it is deposited.

An eighteenth century recipe states that the lampblack is blended along with other carbon-laden powders in “boiled” linseed oil, or in other words linseed oil that has been bodied by heating to drive the water out of the flax seed extract and thicken the oil into various degrees of viscosity, depending on the season, the temperature of the work area, and the type of material to be printed.
To eliminate the oily tars that accompany the lampblack, the mixture was heated in copper cauldrons until fumes arose that burned for a few moments: thus was the so-called “flame varnish” produced. The cauldron was then covered to put out the flames. The very viscous ink that this process yielded, penetrated very slightly into the paper and dried more quickly; to increase its viscosity even further, the makers added rosin to the cauldron.

Even in the eighteenth century, colored inks were rarely used (and in the heroic period of letterpress printing were almost unknown); an anonymous manuscript of 1706 refers to only five colors, prepared by mixing powdered minerals with linseed oil: red, orange, green, sienna and blue. Normally, however, makers limited themselves to producing a bit of red for ecclesiastical books (called “black-and-reds” in the trade because of the two colors of their inks). This red ink was made with linseed oil that had been bodied by heating (which eliminates water and causes oxy-polymerization of the oil molecules, thus forming *macromolecules* with crosslinked chains that become longer and longer as the oil thickens) to which finely ground mineral pigments of the desired color were added. Naturally, the color of these inks varied according to the source, purity and batch of the minerals used, while the latters’ scarcity also made them much more expensive than black ink.
A certain air of alchemy continued to surround ink-making for much of the seventeenth and eighteenth centuries, as exemplified by an anonymous recipe for oily red ink found by the author in a seventeenth century manuscript.
Walnut oil is boiled to thicken it, adding the heavy and enormously expensive ground cinnabar (reddish orange mercury sulfide) grain by grain. A few cloves of mashed garlic are then added (perhaps for the sulfur compounds it contains), and the oil is evaporated until it is reduced to one third of its original volume, yielding a viscous, stable product capable of holding the heavy cinnabar in suspension. Nevertheless, I am convinced that the pigment would eventually settle to the bottom of the container, but the alert craftsman would be quick to solve the problem with the simple method of shaking before use. Such homely methods are often the best, and in those days were likely to be the only ones available.

One of the major sources of information about eighteenth century inks is William Lewis’s *Commercium philosophico-technicum* (Oxford, 1763), which can be regarded as the first scientific investigation of iron gall inks and their preparation.
Adding sugar to iron gall inks, as was done by the inventor and engineer James Watt (1736 -1819), famous for his work with the steam engine, had long been known as a way of improving gloss. Sugar (like honey, dextrin, dextrose and gum arabic) ensures that ink adheres better to the paper and dries more slowly; as a result, adding sugar to ink makes it possible to make a “contact copy” of a document simply by pressing another sheet of paper to it within twenty-four hours of the time it was written. This is the principle behind the “letter copying machine” for which Watt and his partner Matthew Boulton (1728-1809) were issued a patent in 1780.

A formulation of this kind was used in a red ink – *bookbinders’ red* – made from chips of red Brazilian logwood (Heamatoxylum campechianum, once known as the Campeachy tree) left to steep in vinegar for three days, after which the infusion was boiled and filtered. Gum arabic and equal quantities of alum and sugar were added to the extract to give it body and improve the ink's adhesion (the alum, aluminum sulfate, acts as a mordant) to the paper.

Interesting formulations have also come from anonymous compilations of recipes, now in private hands and jealously guarded by their owners, that often come to light by mere chance. The following example is an eighteenth century Piedmontese recipe, found by myself, for a color imitating gold.
Take gum arabic, twelve *grossi* (a unit of weight), and melt it; add one ounce of raw (metallic) mercury and two ounces of ammonium salt (ammonium sulfate). Place the whole in a glass vial sealed in the flame and heat it in an *olla* (an earthenware pot) full of ashes until the salt melts. Then add *orpiment* (red-orange arsenic trisulfide) and brass filings (brass being an alloy of copper and zinc), heating and mixing until the mercury amalgamates with the rest (the vial, we assume, is open, as otherwise it would explode). The result of this procedure, it seems to me, comes nowhere near to resembling gold, but is certain to poison its maker without undue delay.

Towards the middle of the eighteenth century, dyes began to be added to iron gall ink to strengthen its color and make it easier to write with.
Somewhat later (1763), Lewis investigated the extraction of natural vegetable dyes that would be soluble in the varnishes, vehicles and binders used in inks.
He advocated the use of an extract of a tropical American tree, logwood, (*Haematoxylum campechianum* L., 1753), a raw material that was to have major importance in later years. Logwood extract provides a group of reddish dyes that give a purplish tinge to inks.
Lewis's work was followed by the research of the renowned chemist Charles W. Scheele (1742-1786), who addressed the same problems. In this period (and more especially in the subsequent century), increases in metallurgical and mechanical knowledge were applied to the construction of printing presses.

At this point, we will turn to the work of another of printing's pioneers, Alois Senefelder, inventor of lithography (1798) and, above all, of a revolutionary material: lithographic ink.

6. Lithographic ink

There are remarkable parallels between the lives of Aloys Senefelder (1771-1834), to whom we owe lithography, and Johann Gensfleisch, better known as Gutenberg.
If Gutenberg famously pronounced his invention to be “adventure and art”, the same can be said of the sequence of discoveries and inventions credited to Senefelder.
As is often the lot of innovators, the adventure ended in failure for both, though Gutenberg had a harder fate on the whole; the art, on the other hand, manifested itself in both cases through a new power of expression that made printing an inexhaustible medium of communication.

Born in Prague on November 6, 1771, Aloys Senefelder was educated in Munich, which he left to study law in Ingolstadt. After his father’s death, he abandoned his studies and devoted himself to writing for the stage. Unable to have his plays published, he decided to print them himself, and thus started to experiment with copperplate etching.
To practice the reverse writing – writing backwards – that the etching process requires without wasting expensive copper plates, Senefelder hit on the idea of using the stone slabs from the Kehlheim quarries used to pave the streets of Munich as a substitute.
In the copperplate etching technique, the text or drawing to be printed is traced in reverse, as a mirror image, on a copper plate coated with a ground of acid-resistant wax or asphalt varnish. These traced lines cut through the ground, exposing the metal underneath. An acid solution is then applied which “bites” into the exposed metal, but not into the areas protected by the ground, leaving lines sunk into the plate. The plate is then inked and wiped off so that the ink remains only in the etched lines. When the print is made, a positive impression of the reverse image that was traced on the plate will be transferred to the paper: hence the need to write backwards on the plate to produce a legible print.
The story has it that, one morning in July 1796, Senefelder had to write a laundry list. The laundress (Figure 35) was waiting, but he could find no paper, so he used a stone he had polished in order to practice reverse writing, and a greasy ink consisting of beeswax, soap and lampblack that he had made to cover errors he had made in writing so that they would not be etched into the copper plate. Made at low heat, this mixture can be formed into sticks – or lithographic crayons – which can be inserted into a holder and used like an ordinary (though rather large) pencil.
Afterwards, Senefelder was curious to see what would happen if this stone were etched with aqua fortis (dilute nitric acid) for five minutes. He did so, and found that the areas that had been covered with the greasy ink were left in a slight though perceptible relief. He inked them, and was able to pull a print from the stone.
He continued to experiment, and found that when the stone was dampened with an acidic solution containing gum arabic, it became markedly hydrophilic, or in other words absorbed water readily (thanks to the intrinsic porosity of the type of stone used), but would no longer accept ordinary printing ink. The greasy ink he had invented, on the other hand, was repelled by the wet areas, and would adhere to the parts of the stone that had already been inked to produce the drawing.
The chemical explanation for this lies in the fact that greases are nonpolar dielectric materials with little affinity for polar liquids (i.e., whose molecules possess an electric dipole) such as aqueous solutions. This is why an oil or a grease will not mix with water.
Senefelder’s ink can be made almost liquid, and thus brushable, by changing its composition to include a wax solvent such as turpentine. Consequently, the lithographic method is capable of reproducing both drawings – executed with the lithographic crayon – and paintings executed with a brush and this modified liquid formulation, called tusche. Because of this versatility, lithography had enormous appeal for artists, and lithographic prints, either original (i.e., drawn directly on the stone by the artist) or reproductions of existing works, were produced in large numbers.

After drawing or writing with the greasy ink, Senefelder wet the stone with highly dilute nitric acid containing gum arabic to make the non-printing areas more hydrophilic. He then inked the stone with his greasy ink and printed (Figures 50, 51, 52, 53, 54, 55, 56, 57).
Senefelder gradually arrived at true lithography, based on the "chemical separation" between printing and non-printing areas, relying, not on relief as was the case for letterpress printing, but on the different chemical affinity that ink and water show for the image and the bare areas of the stone, separating the image from the stone by means of the chemical antagonism between acidulated water and oily ink.
Alternating wetting, inking and printing, Senefelder achieved an acceptable product in 1798: this was the discovery of a new printing method, which he called "chemical printing" in the account of his work that he published, much after the fact, in 1818.
The inventor also declared that he could produce 6000 impressions a day with three presses, which demonstrates that he had also solved the technical problems involved in making lithographic prints.

Of the many recipes for lithographic ink, I will give two, one from a well-known source, and one anonymous:

- According to the great nineteenth century lithographer Lemercier (owner of the largest lithographic printing business in Paris) ink should by made of 4 parts of yellow wax, 3 parts of tallow, 13 parts of white Marseilles soap, 6 of shellac, and 3 of lampblack.
- An anonymous late nineteenth century Piedmontese recipe calls for: yellow wax, 400 g; tallow, 300 g: shellac, 500 g; gum mastic in drops, 100 g: purified white soap, 400 g: Venice turpentine, 50 g: olive oil, 50 g; lampblack 100 g.

And here is how to proceed for the anonymous recipe.
Melt the tallow in the hot oil, adding the lampblack bit by bit until the mixture is uniform and the consistency of a very thick cream which can be pressed into a block, as if it were butter.
Separately, melt the wax, half of the soap, and the shellac. At this point, the author, worried that an accident might happen, warns that:
"…you should take the material off the stove before it catches fire …the flames will rise higher and higher and you will have to be careful …to dominate them."
The materials must be mixed in slowly *"…throwing in small pinches, waiting until each melts before adding the next …"*
When everything is liquefied, put out the fire and add the rest of the soap, a little at a time. Add the turpentine after the mixture has cooled (to avoid causing a fire) and then mix thoroughly over low heat. Filter to remove tarry residues. At this point, add the block of tallow and lampblack prepared earlier and place over moderate heat, stirring constantly until the mixture is completely melted and uniform. Then pour the ink onto a stone slab greased with tallow, allowing it to cool and harden sufficiently to be cut into tablets for sale or "cast" in brass molds to make lithographic crayons.

G.I. Arneudo, in his *Dizionario esegetico, tecnico-storico per le arti grafiche*, a dictionary of the graphic arts published in Torino in 1917, states that lithographers use three different types of ink: the "fine", higher quality grade for crayon work, a medium quality grade for printing images based on pen and brush work, and a less viscous, lighter grade of ink for printing with fast and more or less automated presses where there would be a risk of tearing the sheets of paper.
Arneudo also says that the lithographic inks used in the late nineteenth century employed varying proportions (depending on the use for which they were intended) of soap, mastic in drops, yellow shellac, virgin wax, saltpeter and lampblack that had been purified to remove salts, resins and oily components.

Senefelder's lithographic method, inks and press remained unchanged until the introduction of offset lithography in 1905; even today, lithography as an artistic medium still uses the same "stone-printing" techniques developed originally by Senefelder. Major changes, on the other hand, have been made for the inks now used in offset printing.

7. Advances in chemistry

In the nineteenth century, advances in chemistry opened up new horizons for ink making. In 1820 Reid, following in the footsteps of Bostok, found that fermentation of tannic acid by a mold produced pure gallic acid, which combined with ferric sulfate yielded an intense black color. After this, attempts were made to eliminate iron salts from ink-making processes, as their oxidation damaged manuscripts.
The famous Swedish chemist Jöns Jacob Berzelius (1779–1848) substituted iron salts with ammonium vanadate (1832), which reacts with gall to produce an indelible black liquid. This liquid, however, was found to fade when exposed to light for prolonged periods.
The first true vegetable dye used in inks was natural indigo (extracted from *indigofera tinctoria),* followed by indigo treated with sulfuric acid and other chemicals to make it more soluble. Potassium chromate began to be added from 1848 onwards: inks of this kind were reddish or purplish when applied, and turned black afterwards.
Other advances were made by Runge (1847), who can be considered the father of modern writing inks. He treated logwood with potassium chromate, obtaining a black ink with neutral pH.
The so-called “alizarine ink” which was to be so successful in the nineteenth century was invented by Eduard Leonhardi (1826-1905), whose patent dates to 1856. Alizarin is a red dye that had been extracted from the madder root since ancient times, and was then reproduced synthetically starting in 1858. Until then, the iron salts used in making inks were held in suspension by the thickening action of gum arabic. Leonhardi introduced a new formula in which the reaction with the iron salt did not take place in the liquid, but on the paper, as a result of the oxidizing action of the air on the salts, which do not react with alizarin. Consequently, there was no longer a risk that the salts would settle to the bottom of the inkwell. Instead of being black, this ink was thus the orangish color of the alizarin dye. On the paper, it would slowly darken as the ferrous salts oxidized into ferric iron, which with alizarin yields a rich, glossy black.

Prussian blue, also called Berlin blue or Paris blue, a synthetic dark blue pigment, was discovered by accident in Berlin by Diesbach and Dippel in 1704, though it began to be used in ink production only towards the middle of the nineteenth century. Chemically, it is *ferric ferrocyanide*, $Fe_4[Fe(CN)_6]_3$.

Many attempts to produce dye-based inks were made, especially in the nineteenth century, but the real breakthrough came in 1856, when William Henry Perkin, attempting to synthesize quinine, happened across mauve, a violet dye derived from *aniline*.
The appearance of aniline colors around 1860 revolutionized the world of dyes, making it possible to produce writing inks based on pure dyes which neither clog the pen nor corrode paper.

For black inks, aniline dyes such as *induline*, *methyl violet* and *nigrosine* were used. For reds, common synthetic dyes include *rhodamine* and *eosin.*
What followed is the history of the modern ink industry, a subject we will return to later.

The new dyes opened the way to many new kinds of “sympathetic” or “invisible” ink, consisting of substances that change color when mixed with an acid or base (*phenolphthalein*, for example, which goes from colorless to purple when exposed to ammonia); many others rely on a full-scale chemical reaction that yield colored salts from colorless writing fluids (the classic example is *cobalt chloride*, nearly colorless, which turns blue with *potassium ferricyanide*).

7.1 Nineteenth century ink-making

The equipment required for ink-making is neither costly nor complicated to operate; essentially, the only things needed are containers for mixing the solid and liquid raw materials, a few filters, and more containers where the ink can be left to age and settle.
The containers used were wooden vats, or even ordinary barrels, when the solid and liquid raw materials were mixed into solution without heating. If heating was needed, cylindrical metal boilers with a slightly concave bottom were used instead of vats. These boilers were made of heavy gauge iron sheet, and could be chromium plated to improve their resistance to corrosive chemical reagents, or enameled if the solutions to be heated contained substances that could be affected by contact with metals.
In certain cases, however, materials could also be heated directly in the wooden vats by connecting a steam generator to them.
Nineteenth century boilers and vats already featured a manual or mechanical stirrer to mix and dissolve the solid raw materials in the liquid solution.
Where small quantities of liquid had to be filtered, ordinary cloth or paper filters placed in large funnels were sufficient. For larger volumes, filter presses were already in use by the end of the century. These units consist of a series of removable wooden or metal frames, each carrying a sheet of high-grade filter paper or cotton canvas. A pump forces the cloudy liquid through each of the frames, which retain the solid matter, and the filtered liquid is collected in a channel below the press.
Care was taken to ensure that the water used for nineteenth century writing inks did not contain salts of iron, manganese, calcium or magnesium: compounds of iron and manganese can cloud certain aniline dyes, while calcium and magnesium salts cause tannin, and many dyes, to precipitate out of solution. Natural waters, however, invariably contain mineral salts, especially those of calcium and magnesium.
Hard waters are far more abundant in nature than soft waters. Before they are used, these waters must thus be softened by means of a treatment that removes most of the calcium and magnesium salts.

Inks are rarely ready for use immediately after they are made; they acquire the desired properties only after a certain period of rest, away from contact with the air, in which a number of complex phenomena occur in a process of “maturing”. Good black writing inks were left to rest for six to twelve months.

In 1818, ink-making was put on an industrial basis when Pierre Lorilleux, printer at the *Imprimerie Royale,* founded an ink factory in Paris. Success came quickly, and to meet the flood of orders he received, Lorilleux was soon obliged to add to the capacity of his first primitive workshop on the banks of the Bièvre at Meison Blanche (1820) by building a second, and far larger, factory on the hill at Puteaux (1824).
In 1823, Savage published a book dealing with all the major methods for making black and colored printing inks, while in 1848, H.D. Wade, a New York druggist, was the first to experiment with mixtures of resins as a partial substitute for linseed oil.

In the meantime, sophisticated metal printing presses appeared on the market (Figure 58), fruit of the period’s improvements in machining techniques.

1816, Angelo Belluschi, a former pressman, set up a small printing ink plant in Via Moscova 37, Milan. Two years later, he hired Camillo Orsenigo, who became a partner in 1829 and owner of the plant in 1850.
In 1857, Camillo’s son Francesco Orsenigo introduced the first three-roll ink mill – a heavy machine with three granite rolls that replaced the mortals and pestles previously used to grind inks. The Orsenigo factory enjoyed considerable fame, not least because it was the only Italian plant to patent its inks. It was equipped with twenty steam-driven machines for making letterpress and lithographic inks. The company also made inks for newspapers printed on reel-fed rotary presses: revolutionary for their day. Prices

ranged from 1 to 2 Lire per kilogram, depending on color. Also highly successful – and, at 20 Lire, highly priced, was the *Tavolozza tipografica* (The Printer's Palette) published by Orsenigo.
In Torino, the first ink factory was founded by Francesco Berra, ex-pressman at the Stamperia Reale. In 1829, Berra displayed several examples of colored and black and white prints made with his own inks at the city's Public Exposition. His work won a medal, though only a bronze one.
In 1831, the "Fratelli Berra" factory applied for a license that would give them exclusive rights to produce inks "by appointment" in the Royal States of Savoy, but the Consiglio di Commercio – the kingdom's board of trade – refused on the grounds that an ink factory already existed …in Genoa! Not exactly next door, perhaps, but how many ink-makers could a self-respecting little state possibly need? Undaunted by this denial, the company continued production, and contributed to freeing Piedmont from its dependence on imported French inks.

By the end of the nineteenth century, the chemical industry produced thousands of kinds of pigments and dyes, and ink-makers had only to choose the ones that would be best for each particular need. To entice prospective customers, ink producers arrayed their wares in chromolithographed labels showing Oriental landscapes and exotic odalisques in entire rainbows of alluring color, which even today have lost none of their appeal.
Then as now, pigments were chosen for their hue, saturation, purity, lightfastness, and insolubility in water and oils (Fig. 59,60,61,62,63,64,66,67,69,70,71,72,79,83).
Other properties depend on the varnishes and vehicles used, and include their ability to ensure that the ink has the right consistency (the right amount of body and tack), can produce a good, glossy print, and has sufficient abrasion resistance.

7.2 A brief digression on metal pens and nibs

Metal pens have also had an importance of their own in the development of writing and the history of ink. Metal pens have very early origins, though the exact date of their invention is not known. Naturally enough, the encyclopedia *Larousse*, practically a French national institution, patriotically states that the metal nib was invented in the second half of the eighteenth century by a French mechanic, one J. Arnoux. In the English-speaking world, the magazine *Cosmos*, in its issue of September 15, 1900, assigns credit for the invention to the American Peregrine Williamson, a jeweler, around 1800. The Germans also claim paternity of this tiny but nonetheless important instrument, attributing it to a schoolteacher in Koenigsberg named Burger, who published an account of his new contribution in 1808. But the Englishman James Perry came to hear of the invention, and took out a patent for it in 1830. As compulsory education spread throughout Europe and beyond, millions of Perry's steel nibs were sold around the world, and he quickly became a millionaire.

The metal pen, with its replaceable nib slipped into a holder, completely superseded other writing implements because of its inherent advantages The nib is flexible and long-lasting, and can be made in different shapes and styles to imitate ancient forms of calligraphy or invent new ones. Steel nibs were the most economical, though they tend to rust. This is a problem that nickel-plated nibs (the humble nickel looks like gold) do not have, while bronze or chromium-plated and stainless steel nibs were also in considerable demand, thought their prices are obviously higher. British brands were among the most important, and were widely available even in Italy: our grandparents could name such famous nib makers as *James Perry, John Mitchell,* and *Hinks Wells & Co*. Well-known French products included those by *Blanzy-Poure, Baignol & Fairon, Mallat,* and *Conté*, while the Germans could boast *Heinze & Blankertz* of Berlin, *Brause & C.,* and *Soennecke* of Bonn (Figures 65,68,73,75,80,81,82,84,86,88).

In the Italy of the 1920s, prominent metal pen makers included *Presbitero, Legnani, Ruspi, Locati* and *Fiore*. Each producer had a series of exclusive models, each identified by its own trademark. Ruspi, for example, offered the *Astoria, Cobaltea, Elettra, Trionfo,* and *Sahara* lines, while Legnani models included the *Freccia d'oro, Gloria, Littorina, Serpentina, Impero* and *Lux*, names redolent of the Fascist period. Some of these pens are amusing because of their odd shape: the "penna reale", for instance, impressed with a royal crown, or the "penna antonelliana", modeled after Torino's Mole Antonelliana, symbol of the city and most prominent feature of its skyline.

Many other makers served the large market for metal nibs. And then came the 1950s and the unstoppable rise of the ballpoint pen: unstoppable despite its early ban from elementary schools, where fledgling penmen were still required to leant to "write in ink"!

7.3 New writing implements

A pen that would not have to be dipped continually in the inkwell is a very old idea. The first historical record of a pen carrying its own supply of ink dates back to the tenth century. We are told that in 953 AD, the caliph of Egypt demanded a pen that would not stain his hands or clothes, and was provided with a pen which held ink in a reservoir and delivered it to the nib via gravity. Obviously enough, this is all we know of this pen.

Documented attempts to construct a reservoir pen are far more recent: drawings by Leonardo da Vinci show a pen with an ink chamber that has been reconstructed in modern times on the basis of these few sketches. Some scholars maintain that careful analysis of the writing in Leonardo's codexes shows it to have a regularity and continuity that could not have been achieved if the pen had had to be dipped in the ink every few moments; the same is true, they say, of the many ink drawings that illustrate the codexes. It is thus not too far-fetched to conclude that Leonardo did in fact make a reservoir pen, and used it in his work.

In his *Delicia Physic-Mathematicae*, the German mathematician, inventor, poet and librarian Daniel Schwenter (1585-1636) describes a pen made from two goose quills, where one quill served as a reservoir for ink inside the other quill. The ink was sealed inside the quill with a cork, and was squeezed through a small hole to the writing point.

Pens of this kind were produced in the seventeenth century, but none survive. Progress in developing a reliable pen was slow, however, until the mid-nineteenth century, largely because of the very imperfect understanding of the role played by air pressure in the operation of reservoir pens, and the fact that inks were still highly corrosive and full of sedimentary inclusions.

The modern history of the fountain pen began in 1780, when a certain Scheller made a bronze and horn prototype of which little is known; it was not until 1827 that the French government issued a patent for a reservoir pen invented by a young Romanian, Petrache Poenaru (1799-1875), physicist, engineer and designer of Romania's current tricolor flag, who was then studying in Paris.

Starting in 1850, there was a constant increase in fountain pen patents and the number of pens in production. It was only after three key inventions, however, that the fountain pen became a widely popular writing instrument: the iridium-tipped gold nib, free-flowing ink, and the hard moldable rubber, or *ebonite*, used for the pen barrel and developed by Charles Goodyear and Thomas Hancock in 1843 through the prolonged vulcanization of a mixture of natural rubber and sulfur.

In 1870, Duncan MacKinnon, a Canadian, made a stylographic pen with a hollow, tubular nib and a wire acting as a valve: a technique adopted for the pens employing India ink which were long used for drafting and technical drawing. Mass production of these writing instruments began towards the end of the century, when they became a popular status symbol.

In this period, fountain pens were filled by unscrewing a portion of the hollow barrel or holder and inserting the ink by means of an eyedropper. This was a slow and messy system. Fountain pens also tended to leak inside the caps and at the joint where the barrel opened for filling. The problem to be solved was that of creating a simple, convenient self-filler that would not leak.

The modern fountain pen contains a reservoir of liquid ink which is supplied precisely and constantly to the nib by means of a feed system which operates through a combination of gravity and capillary action. Ink can be delivered to the nib from pre-filled cartridges or a mechanism similar to an eyedropper, or by using any of a variety of ingenious systems. Most fountain pens use disposable ink cartridges or a reservoir filled with a screw or piston mechanism (Figures 95, 96).

For the more costly models (an expensive fountain pen is always a status symbol), chrome steel nibs are replaced by wear-resistant iridium tipped gold or even platinum nibs. Fountain pens, once among the most common of writing instruments, have been produced in innumerable designs, ranging from the starkly ergonomic to the lavishly luxurious.

i)

ii) A number of formulas for fountain pen inks (as indicated by the 1965 edition of the classic Italian chemistry reference, the "*Nuovissimo ricettario chimico*") contain varying percentages of glycerin, ethylene glycol and distilled water in addition to dyes such as methyl violet, nigrosine and so forth. There have been no important changes in this area in recent years, as the advent of new writing implements such as ballpoint, rollerball and felt-tip pens has caused consumption to drop sharply. Nevertheless, bottles of fountain pen ink are still sold, and the elegant ink bottles of bygone days have, like bottles of vintage wines, become prized collectors' items, proudly displayed in glittering showcases (Figures 90, 91, 92, 93, 94, 97, 98, 99).

7.4 The ballpoint pen: revolution of the spheres

The history of the ballpoint pen had a definite beginning, if we look only at documented patents. How and when the idea arose, however, is open to debate.

In 1888, John Loud, an American tanner, patented several types of marking pen featuring an ink reservoir and tip containing a small rotating ball that applied thick ink to leather hides. John Loud's pen was never produced or used for writing on paper. A replacement had yet to be found for the fountain pen and its ink that tended to smear if the writer was too fast: a problem much decried by the movers and shakers of the bustling industrial age.

In 1891, a similar patent was filed by a certain Edward Lambert. The ballpoint pen we know today, called a *biro* in many parts of the world, owes this name to its real inventor, the Hungarian journalist *László József Bíró* (1889-1985). Birò first tried to eliminate the problem of smudging encountered with fountain pens by replacing the ink with the fast-drying type used to print his newspaper. Printing ink, though, was thick and hard to write with, since it would flow into the fountain pen's nib barely, if at all. So

Birò had another idea: fitting a tiny metal ball in a socket on the tip of the pen, which would thus distribute the ink more evenly on the paper. It is said that the idea came to Bíró from seeing a soccer ball roll through a puddle and leave a wet stripe on the asphalt.

Birò's experiments were interrupted by history: the Second World War was looming on the horizon, and Birò, together with his family, fled first to Paris and then to Argentina. Here he began to produce his pen with the help of various experts: to operate correctly, it needed a metal ball with very precise dimensions that could only be supplied by a Swiss company. Another problem was that of developing an ink with the right viscosity: initially, this was an area where Birò was assisted by his brother, György. In 1935, Birò patented his pen in Hungary.

In the same year, Frank Klimes and Paul Eisner were the first to put a ballpoint pen on the market: the *Rolpen*. In 1939, Biro tried to produce his pen in France, but was forced to stop because of the war. It was not until 1943 that he was able to patent his invention and, financed by Henry Martin, started to produce it in Argentina as the *Stratopen*. In 1945, the Italian baron and naturalized French citizen Marcel Bich (Torino 1914 –Paris 1994) bought the Birò brothers' patent and began to manufacture pens in small batches, as he did not yet have the technology to improve the produce and make it mass-marketable.

Bich, born of a noble family from Italy's Valle D'Aosta who had moved first to Torino and then to France, created an industry to which he gave his own surname, minus the final 'h': Société Bic. He perfected the ballpoint and sold it, in ever-increasing volumes, around the world: it was perhaps the first example of the disposable consumer goods that have become such a feature of modern life. Bich had two other ingenious ideas: the disposable razor and the disposable cigarette lighter. Today, and every day, millions of people around the world write, shave and light their cigarettes with Marcel Bich's economical and extraordinarily practical inventions.

The first great commercial success for the ballpoint pen came in October 1945, when Milton Reynolds sold his pens at Gimbels Department Store in New York. A crowd of over 5000 people jammed the Manhattan store's entrance: astutely, Gimbels had taken out a full-page ad in the *New York Times* the day before to promote the first sale of ballpoints in the United States. The ad described the new pen as a "*fantastic...miraculous fountain pen... guaranteed to write for two years without refilling*". On that first day of sales, Gimbels sold out its entire stock of 10,000 pens – at the hefty price of $12.50 each.

Bich became enormously wealthy, while Birò died poor in Buenos Aires in 1985; Argentina, however, celebrates "*Inventors' Day*" on Birò's birthday, September 29.

The ballpoint pen consists of an internal chamber (or refill) filled with a viscous ink that is dispensed at the tip by the rolling action of a small metal sphere between 0.1 mm and 1 millimeter in diameter; the more economical pens have larger diameter spheres. The sphere may be steel of tungsten carbide, or even, on the more expensive models, sapphire. The chamber holds from 0.4 to 0.6 grams of extremely viscous ink, which in theory is enough for a line 15,000 to 16,000 meters long. The ink dries almost immediately after contact with paper (Figures 100, 101, 102).
Inexpensive, reliable and maintenance-free, the ballpoint has largely replaced the fountain pen.

Ballpoint pen ink must be thick enough not to run, or in other words leak past the metal tip and cause stains when the pen is set down somewhere or put in a pocket. It must write smoothly, but not migrate through the paper and be visible on the other side of

the sheet. It must also stay at the right viscosity, even after the pen has been used for hours or when the temperature changes.
In addition, the ink acts as a lubricant for the metal ball. The coloring agents it contains are soluble in oil: alkaline dyes dispersed in fatty acids, acid dyes such as nigrosine – economical, but tending to break down under UV light – and the more lightfast phthalocyanines and methyl violet, as well as pigments or graphites dissolved or suspended in a sufficiently viscous vehicle.
The vehicle may be a high molecular weight alcohol, an ester, mixed with small amounts of natural or synthetic resins. Until around 1970, vehicles contained olein (oleic acid), though this is no longer used today because of its tendency to oxidize, polymerize and stop flowing. Currently, esters such as isostearate (glyceryl) or oleylsarcosinate, which do not oxidize and block the flow, are used together with glycols and polyglycols that are not subject to oxy-polymerization, and may be combined with stable synthetic resins.
An important innovation has recently been introduced: oil-based inks have been replaced by highly fluid gel inks which write very smoothly, much like a fountain pen. These inks have gained a large market: though fluid, they do not drip because of their carefully controlled use of *thixotropy*. This thixotropy means that the ink becomes very viscous when the pen is not being used, but its viscosity drops abruptly when the pen starts writing. The phenomenon is caused by the change in velocity that the pen undergoes in writing, and is made possible by special “associative” polymers contained in the ink.

7.5 A new way of writing: fiber tip pens

Fiber or felt tip pens first came on the market over thirty years ago. They use low-viscosity ink that flows readily through the capillary network formed by the *sintered* (i.e., bonded together by partial melting) polyester fibers that form the pen’s tip. If their fluidity and drying properties are well balanced, the inks used in these pens write smoothly and produce clean, crisp lines in a variety of widths, depending on the size of the tip. These inks now consist of water-based solutions of dyes that are safe for children. Adding *high boiling* liquids such as ethylene glycol to the ink formulation prevents the tip from drying out, extending the pen’s life.
Permanent markers, on the other hand, use inks with an alcohol-based vehicle and can write on virtually any surface, making markings that cannot be washed off with water. Tip sizes vary from the ultra-fine *microliners* to the wide-tip markers used for signs and posters.

Inks general consist of acid or basic dyes in an alcohol base. More rarely, they may employ grease-soluble dyes in a base consisting of a nontoxic hydrocarbon. Both types contain a resin, which must be soluble in alcohol in the first case and in hydrocarbons in the second.

Highlighters, a more recent invention, are also widely used. They contain fluorescent dyes that do not photocopy well in normal copiers because of their high *reflectance*: they reflect the light beam moving across the paper in the machine, and thus show up on the copy as almost white.

Another type of fiber tip marker is the *whiteboard marker* or *dry-erase marker* used on the painted or plastic coated whiteboards that have replaced chalkboards in many schools. Whiteboard makers can be erased with a cloth, without creating the clouds of chalk dust that once hung so long in the classroom air.

8. New printing inks

To round off this brief history, we will also devote a little space to contemporary inks, though their variety and complexity deserve far more attention than can be devoted to them here.
In the late nineteenth century, the introduction of triple roller ink mills with granite – or even harder jasper – grinding rolls had made it possible to produce much finer pigment pastes. By the turn of the century, according to Arneudo, the finest and highest quality printing ink was ground ten or twelve times.
Once the hand press had been abandoned, flatbed cylinder presses were first supplied with sheets manually. Later, towards the end of the nineteenth century, they were equipped with mechanical automatic feeders that sped up production and made presses safer to work with. This, however, made it necessary to develop faster drying inks to prevent "set-off", or in other words the transfer of ink from one sheet to another when they are stacked at the delivery end of the press.

Where a single formula had once been sufficient, many different types of printing ink were gradually developed for different impression techniques and different types of work, using, for instance, higher viscosity formulations for sheet-fed presses and lower viscosity inks for the faster web-fed machines.
Inefficient mineral pigments were abandoned in favor of synthetic pigments for colored inks. For example, inorganic mineral pigments have been replaced by organometallic pigments such as copper phthalocyanine, which have higher chromatic intensity, produce more uniform colors, are lighter in weight, and are compatible with a wide range of vehicles.
The major thrust of research and development work has shifted away from writing inks, to concentrate to a much greater degree on printing inks and the methods for producing them.

After 1930, new resins derived from polymers synthesized from petroleum products were used for varnishes and binders. Vehicles made with these novolac phenolic resins have more consistent properties than those produced from natural substances, which can vary significantly according to source and age.
Following the Second World War, synthetic resins made enormous steps forward, becoming the basis of all printing inks.

Even with all these changes, the history of ink is sometimes one of continuity. Armando Maloberti of the ink factory of the same name tells me that in the 1930s, the last descendent of the Orsenigo family, Camillo, was the driving force who enabled the well-known Paris ink producer *Lorilleux-Le Franc* to expand its Italian business. He made a fundamental contribution to setting up the Lorilleux facilities in Via Benigno Crespi, Milan, where the company remained until it relocated to Senago in the 1970s. Lorilleux continued its growth in Italy by absorbing Battistini's equally well-known company, *Cometa S.p.A.* (Figures 74,76,77,78,85,87,89).

More recently, *Lorilleux* formed an alliance with the British maker *Coates* in the late '80s. The Coates Lorilleux partnership was then acquired by *TotalFina*, which also bought the *Colorama* group. At the end of the last century, Coates Lorilleux merged with *Sun Chemicals*, a wholly-owned subsidiary of Japan's *Dainippon*.

8.1 High-viscosity inks

Inks with a highly viscous vehicle, known in the trade as "paste" inks, have been used from the beginnings of printing down to our own day. They are still extremely important, as they include letterpress inks, offset inks and gravure inks.

To give a brief description of how these materials work, we can say that the film-forming portion of the ink laid down on the paper, which consists of the various kinds of synthetic resin that make up the varnish, stratifies and solidifies instantaneously, “trapping” the pigments. The volatile components, on the other hand, are absorbed by the paper fibers and then released more slowly.
Letterpress and offset ink formulas differ in several respects: offset inks do not contain certain pigments that bleed as a result of the dampening used in offset printing, while their varnishes cannot contain components that tend to form oil and water emulsions.

Polychrome prints are produced using the three basic printing ink colors: yellow, magenta (a purplish red) and cyan (blue-green), which can be combined together to provide a full range of colors through “*subtractive synthesis”*.

Obviously, a modern ink is made up of many different ingredients. Once the pigments and dyes have been selected, and the resins for the varnish, it will be necessary to determine the relative proportions that will be needed to produce the desired color and the right amount of body (viscosity) for the printing method that will be used. A variety of dispersants, wetting agents, viscosity modifiers, plasticizers, driers, surfactants and biocides must them be added.

Because of their high speeds, modern presses require inks that retain a certain amount of body, but have less tack to prevent problems such as picking, i.e., lifting and pulling the paper surface, that could result in tearing with the cheaper and thinner stocks used today. Gelling agents and rheology modifiers are thus used, either as components of the ink or added at the time of printing.

Polydispersed varnishes are used to ensure that the ink dries quickly – almost instantaneously – on the paper stock. When these varnishes hit the paper, they separate into two parts, a fluid and a binder. The solvent-based fluid penetrates into the paper’s pores through capillary action, while the binder or film-forming portion of the ink, which consists of hard resins, quickly thickens to form a compact, but not entirely dry, layer. We thus have a form of “selective penetration” that causes the ink to set rapidly; drying will be completed in a few hours without ink set-off or blocking, i.e., the problem where the printed sheets stick together.

Fast web-fed offset presses use heatset inks: the freshly printed stock passes through a heating unit that emits infrared radiation which is absorbed by the varnishes and binders used in these inks, drying them by evaporation.

8.2 Low-viscosity or “liquid” inks

Like their paste counterparts, liquid inks also consist of resin and solvent vehicles containing pigments and dyes that produce the desired color. They include rotogravure inks, used in printing large runs of illustrated magazines and wrapping paper, and flexographic inks, used for newspapers, packaging, flexible plastics and metal foils. Both types share certain characteristics. The first and most important of these characteristics is that they must be based on volatile solvents so that they can dry by rapid evaporation. Consequently, the binders are liquids, though dense ones.
The solvents used in the two types of ink differ: xylene (an aromatic hydrocarbon derived from petroleum) and ethyl acetate for rotogravure inks; ethyl alcohol and water for flexographic inks. The non-aqueous solvents are recovered and recycled.
The properties required for the pigments used in liquid inks are essentially the same as for other inks: lightfastness, resistance to solvents, and resistance to oils and fats (the latter is particularly important for inks used on packaging materials in contact with foods).

Other important properties for pigments include fineness, softness and dispersability in vehicles. The most commonly used pigments for rotogravure inks are benzidine yellows and phthalocyanine blues. For blacks, the basic pigment is still lampblack.
For flexographic inks prepared with dyes dissolved in alcohol, a fixative such as synthetic tannin and/or lacquer is usually added to improve adhesion to the substrate or prevent bleeding if it gets wet.
For many decades, flexographic printing meant printing with aniline dyes: the process, in fact, was called aniline printing. The inks were often prepared at the time of use by the printers themselves. This was not necessarily complicated: for example, the printers could take 10 kilograms of ethyl alcohol and dissolve around 2 kilos of Victoria blue in it, shake vigorously, and they had their ink.

Hot air or infrared (IR) radiation are used to speed up drying and make sure it is complete. For the resins used in these inks, the main requirement is good solvent release, as otherwise the ink could not be used on fast machines. A thin coating of overprint varnish is often applied to the printed material after the ink has dried to protect it and improve appearance.
The utmost attention must be devoted to ensuring that the dried ink film is resistant to abrasion. Abrasion resistance depends on how well the pigment is coated by the binder, or in other words, the pigment's wettability.

The ink's runnability – or in other words, how well it interacts with the press and the substrate – and perfect pigment dispersion are key properties that ensure that the ink can be applied evenly and continuously. Another important consideration is the fact that solvents may be toxic, and must thus be recovered after evaporation and recycled rather than being released into the environment.

8.3 Screen printing and engraving inks

Screen printing and engraving are printing methods that are now largely restricted to the fine arts, where both are widely used, and to special applications: engraving is employed for banknotes, stock certificates and the like, while screen printing is used for premium packaging and to print on non-flat surfaces.
Screen printing inks and engraving inks dry by oxidation and polymerization, or in other words, slowly. Four to five hours after printing, they have set sufficiently to allow the prints to be handled. Complete drying takes two or three days. The varnishes for these traditional inks are made with drying oils (linseed oil, wood oils, etc.) and their derivatives (lithographic varnishes, glycerophtalic resins), plus phenolic resin binders and lead, cobalt or manganese driers.
Screen printing inks have recently been developed that dry by photopolymerization with brief exposure to ultraviolet (UV) light at a calibrated radiation wavelength. This has made it possible to increase the range of applications for screen printing, which has always been appreciated for the excellent colors and high quality it can produce.

The thickness of the ink layer deposited on the substrate with screen printing is approximately ten times greater than with offset printing: several hundredths of a millimeter, and in some particular cases – fine art reproductions, for example – it may be as much as one tenth of a millimeter.
Screen printing inks are used to print on a wide variety of materials: paper, cardboard, wood, leather, cloth, metals and rigid and flexible plastics.

Other so-called "synthetic" screen printing inks are available which are based on vinyl or cellulose base binders dissolved in solvents. These inks dry by rapid evaporation in only a few minutes.

Recently, inks based on hard epoxy resins have been developed which yield prints with high surface gloss and mechanical strength.

8.4 Specialty inks

There is an incredibly variety of inks that are used only for special or limited purposes and are thus not widely known, which we will mention here because of their intrinsic interest.
Luminescent inks, for instance, reflect light in a particular way. They derive their essential properties – *fluorescence* or *phosphorescence* – from the pigments they employ.
Fluorescent pigments make the print brighter because they also reflect the (invisible) ultraviolet components of the spectrum in visible light, an effect which ceases when the pigment is no longer excited by light. Phosphorescent pigments, on the other hand, continue to be luminescent, i.e., emit light, even after the exciting cause has been removed, because they return the light energy that was accumulated during exposure. The vehicle used for the pigment must be such that it does not interfere with this phenomenon. Phosphorescent pigments have a rather large crystalline grain size, and in practice can thus be used only in screen printing inks. By contrast, fluorescent organic pigments are fine, soft powders and can be used to produce writing inks (as used in fiber tip pens and highlighters) and in offset inks for printing brilliantly colored posters.

The panorama of inks in current use is so broad and complex that we can do little more than list them here.
There are moisture-set and steam-set inks, that dry and bind to the paper by precipitation when exposed to water or water vapor, two-tone inks, copy inks and security inks for checks and banknotes, liquid and powder toners for photocopiers, magnetic inks that can be recognized by electronic reading equipment, metallic inks in many different colors, as well as iridescent and pearlescent inks, liquid ink-jet inks for fast printers, waxy sublimation inks for slower printing processes, scented inks, and so on, almost endlessly. Obviously, these inks are protected by patents, and the technological complexities involved in their formulations are difficult for the non-specialist to grasp (fig. 103,104,105).
Thus, the chemical composition of these mixtures and specific functions of their components are beyond our scope here, which is essentially to provide a brief, though necessarily technological, history of ink.

Conclusion

To conclude this study, which has proved far more engrossing than I would have thought possible at the outset, I would like to quote a thought expressed by the Benedictine novice Adso in Umberto Eco's *The Name of the Rose*, because it conveys the noblest function that ink can fulfil: passing on knowledge, and preserving it even in the most tragic moments of history.

"… for centuries and centuries men like these monks have
seen the barbarian hordes burst in, sack their abbeys,
plunge kingdoms into chasms of fire, and yet
they have gone on cherishing parchments and inks,
have continued to read, moving their lips over words
that have been handed down through centuries and
which they will hand down to the centuries to come."

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Historical and bibliographical summary

The major historical treatises dealing with pigments, inks and the like are briefly described below.

Third to Fifth Century

Leyden Papyrus. The oldest extant manuscripts dealing with chemistry and alchemy date from the end of the third century. They are the celebrated Leyden papyrii. That which is most concerned with chemical knowledge, according to the nineteenth century chemist Berthelot, is the Leyden Papyrus X. This document was written in the third century AD and was found at Thebes: it contains large collection of recipes for alchemical and chemical operations, including gilding, silver plating, purifying metals and alloys, making purple dye, etc. These recipes are a starting point for ink and paint chemistry.

The ***Papyrus Graecus Holmiensis*** or ***Stockholm Papyrus*** is an Egyptian papyrus dating from the late third century or early fourth century AD, written in Greek and preserved at the Kungliga Bibliotek in Stockholm. This document is particularly important because it is the earliest surviving example of an alchemical text and, as such, is the oldest record we have of chemical practices and procedures. The papyrus was probably written in Thebes, and was discovered in a tomb in the nineteenth century. It was later transferred to Stockholm.

The Stockholm Papyrus provides a rich, though fragmentary, panorama of technical knowledge in Egypt and the Mediterranean in a period of transition between the classical era and the Middle Ages, though scholars believe that the procedures it describes are often far more ancient than the papyrus itself, and were passed down from generation to generation. The papyrus contains 159 recipes or chemical procedures, in no particular order (in practice, there are 155 recipes, as 4 are repeated), and the topics it covers include alloying silver, the use and fabrication of precious stones, and cloth. Much of it is symbolic or esoteric in nature, often reflecting the first, contemporary, alchemical doctrines, as exemplified by several procedures for creating or imitating gold and silver.

Seventh Century

Isidore of Seville, ***Etymologiae****.* Isidore, seventh century bishop of Seville and son of the governor of Carthage, wrote an enormous folio volume that compiled much of what had survived of classical learning in a sort of rustic encyclopedia. Book XIX has a section on colors, describing most of the lacquers mentioned by Pliny, chrysocolla (a native greenish-blue copper silicate), and purple.

Eighth and Ninth Centuries

Lucca Manuscript 490 or ***Codex Lucensis 490*** in the Biblioteca Capitolare Feliniana of Lucca is a miscellany manuscript copied between 787 and 816 whose contents include a section entitled *Compositiones ad tingenda*, or Recipes for Coloring. The oldest records of the colors used in the Middle Ages are thus found in this eight century manuscript, which can be regarded as a vital link between compilations of the recipes used by artists and technological formularies.

It describes formulations based on cinnabar, litharge, ceruse, verdigris and orpiment, along with methods for coloring mosaic glass and dyeing leather and cloth purple and green. Procedures are given for preparing pigments and gold or silver inks, for coloring artificial stones, for dyeing hides and fabric, for gilding and for working metals and alloys.

It preserves miscellaneous recipes intended for teaching purposes, together with several ancient treatises such as Pythagoras's *Ars numeri*, a fragment of Pliny on the division of time, and a method for calculating Easter. It is written in barbaric Latin, heavily influenced by Greek: a clear sign of its links with similar compilations of recipes from the Hellenistic period. Unlike other such compilations, it is unique, in the sense that only one copy exists.

Tenth and Eleventh Centuries

Mappae Clavicula, tenth century. A miscellaneous collection in Latin of around 300 technical procedures for various crafts and arts. The oldest copy dates to a period between the end of the eighth and the beginning of the ninth centuries, and is one of the oldest catalogs of recipes that has come down to us. Most of the recipes deal with procedures for preparing colors and transforming metals. Many of the recipes from the *Compositiones ad Tingenda* are reproduced. The colors mentioned are all mineral in origin, while gilding and dyeing are also covered.

Though several of the recipes in the *Mappae Clavicula* have been shown to come from the Leyden or Stockholm papyrii, some four centuries earlier (fourth century), the material in general is highly assorted, showing the influences of many different cultures: Greek (Dioscorides), Roman (Pliny the Elder), Byzantine, Arab and British. Other recipes contained in later codexes are carried over from the Lucca Manuscript, though in different order.

De coloribus et artibus romanorum by Heraclius or Eraclius. An important source for the history of dyes, pigments and the technical arts in general. The second section is entitled "*On the use of the fresh juices of plants in miniature painting*", and provides detailed descriptions of how to prepare colors for illuminations and inks.

The introduction speaks of the lost arts of ancient Rome, whose memory should be kept alive throughout Europe: the author proposes to reveal them in his book, which must thus be jealously guarded by whoever comes into its possession.

Heraclius's text consists of three parts, two of which are older, possibly dating from the eight century, and are written in Latin hexameters. The third section is in prose, perhaps from the twelfth or thirteenth centuries. A fragment of this text with sixteen recipes was found in Germany and can be dated to the eleventh century. Heraclius was probably a monk and, as has been suggested, lived in the Venetian territories in northeastern Italy.

The colors described for use in illuminating manuscripts (red from ivy, green from artificial and plant sources, orpiment for yellow and as a substitute for gold) are typical of eighth-century Italy, and of the northeastern part of the country in particular. These recipes are invaluable in helping us understand how medieval craftsmen made their works of art, how they created and applied their colors, and how they achieved particular effects. This collection devotes particular attention to literary form, showing the influence of concepts we also find in Vitruvius, Pliny the Elder and Isidore of Seville.

Eleventh and Twelfth Centuries

Theophilus Presbyter. Judging from his clear, detailed descriptions of the medieval arts, Theophilus, known as Theophilus the monk, must have been a practicing craftsman, and indeed a master of his craft, as well as a writer. His writings are more complete and orderly than their predecessors, and reflect all the richness and variety of Romanesque art and culture, as well as providing valuable insights into the history of medieval chemistry.

L'Escalopier's translation divides the text into three books: the first deals only with colors, and how they are used and applied to various types of surface. It describes how to prepare many pigments, including ceruse, Spanish green or verdigris, cinnibar, minium, and others. Theophilus teaches the reader how to prepare glues to fix pigments, and is the first to recommend using linseed oil in paints.

Thirteenth Century

Petrus de Sancto Audemaro or Pierre de St. Omer, a monk from Northern France and near-contemporary of Theophilus, wrote "*De Coloribus Faciendis*". He describes how to apply pigments to books, or in other words in illuminations, using gums or egg white. The manuscript contains the usual recipes for colors, inks and gilding. The colors mentioned include green, prepared in various ways from copper and from plants, white from lead, black from soot, blue from copper and plants. The red pigment was artificial vermilion, red lead, which the author calls minium or sandarac. His only yellow pigment was saffron, though this was used mostly for lacquers and varnishes.

Fourteenth Century

De Arte Illuminandi. As the title implies, this text deals only with manuscript illumination. It was found in 1872 in the Biblioteca Nazionale of Naples and is the work of an anonymous late fourteenth century Italian illuminator. It describes methods and recipes used personally by the author.

Fifteenth Century

Il Libro dell'Arte o Trattato della Pittura – The Craftsman's Handbook – by Cennino Cennini da Colle Valdelsa, was first published by Giuseppe Tambroni in 1821. Cennini's life spanned the late fourteenth and early fifteenth centuries, and his book deals principally with how colors were prepared at the end of the 1300s. Tambroni's edition of the treatise was published in a number of languages, while corrections were added by Carlo and Gaetano Milanesi in the Le Monnier edition of 1859.

Jan van Eyck (1386-1440). Van Eyck is often credited with inventing oil painting somewhere around 1410, though Theophilus, writing in the twelfth century, already gives a clear description of grinding pigments with linseed oil. Before van Eyck, however, the linseed oil was used raw, and painters had to endure tedious waits between coats because of raw linseed oil's slow oxy-polymerization.

Bolognese Manuscript *or* ***Segreti per colori***. The "Secrets of Colors", a fifteenth century manuscript now conserved in the library of the University of Bologna, provides us with an idea of the state of chemistry in the Italy of that day; among other dyestuffs, it mentions and describes the use of indigo. The work is divided into eight chapters; it discusses blue, and lapis lazuli or ultramarine blue in particular, and the various ways of producing it. In the third chapter, after describing how to make blues with the juices of several plants, it discusses methods for making indigo from woad. The fourth chapter teaches a number of ways of preparing verdigris or copper green.
The fifth chapter contains recipes for making a number of lacquers, while the sixth describes preparing purple or mosaic gold – *aurum musivum*, or stannic sulfide – with mercury, with tin (Venetian or Roman) and with sulfur, in various ways but similar to those described in *De arte illuminandi*. The seventh chapter gives several methods for preparing cinnabar with quicksilver (mercury) and sulfur, and the eighth chapter deals with dyeing a variety of materials.

Sixteenth Century

The sixteenth century was a period that saw major advances in oil painting. In Italy, the first true technical treatises dealing with all aspects of the arts were published. With the discovery of the Americas and the West Indies trade route, cochineal and indigo began to be imported, opening up a whole new range of possibilities for the color and dye industry.

Venice became a center for the preparation, purification and use of many pigments and dyestuffs; it was there that all of the colors needed in book decoration, writing and dyeing were prepared. The best indigo from India and Egypt arrived in Europe by way of Venice.

Venice also carried on a busy trade in cobalt blue, discovered by Schurer in 1565. Ceruse, or lead carbonate, was made in Venice and was thus known in the business as “Venetian white”.

Venice produced large quantities of many chemicals used in dyeing and painting – alum, for instance, and turpentine, which was thus often known as Venice turpentine. In addition, Venice was renowned for the colors used in enameling, mosaics and glassmaking.

Dyeing in Venice*: “Libro di tintoria intitolato Plicto, che insegna a tenger panni, tele, bombasi, & sede, si per l'Arte maggiore come per la comune. Nuovamente stampato e ricorretto*, in Venetia, appresso Lelio Bariletto, 1565 (1540). (The Plichto or Book of Dyes, which Teaches the Dyeing of All Manner of Woolen, Linen, Cotton and Silk Stuffs, by the Great Art as Well as by the Common, Newly Reprinted and Corrected, in Venetia, at the printworks of Lelio Bariletto, 1565 (1540). Though not indicated on the title page, this marvelous book of dyeing “secrets”, a true treatise on color chemistry, is known to be the work of Giovanventura Rossetti, a craftsman at the Venice arsenal who already had a claim to fame as the author of another “book of secrets”: *Notandissimi secreti dell'arte profumatoria*, or Useful Secret’s of the Perfumer’s Art (Venice, Francesco Rampazzetto, 1555). The *Plichto* is divided into four sections, in which a total of 225 recipes for dyeing fabrics and many other materials are minutely illustrated.

I Secreti del Reverendo Donno Alessio Piemontese. Work of the versatile sixteenth century writer Girolamo Ruscelli (under the pseudonym of Alessio Piemontese, often latinized as Alexius Pedemontanus), the *Secrets* went through many editions and was translated into a number of languages: Ruscelli was possibly a physician, or an amateur of the natural sciences and an alchemist. He spent many years traveling, gathering a quantity of recipes, formulas and procedures. He discusses illuminations, the preparation of various chemicals from minerals, how to imitate ebony, mordants, the many methods for painting metals, inks for writing and printing, and ways of preparing corrosive sublimate (mercuric chloride), cinnabar, and much more.

Théodore Turquet de Mayerne (1573-1655). Swiss-born, Mayerne was educated in Montpellier and Paris, and later in Germany and Italy. A follower of Paracelsian theories, he endorsed the use of chemical remedies. He was physician to Henri IV of France, and later to James I and Charles I. While living in England, Mayerne developed an interest in painting, and made extensive studies of the materials used in that art. He wrote a treatise on pigments for painters, and it appears that he learned the method for preparing them from the renowned portraitist Van Dyke, whom he numbered among his friends.

Seventeenth Century

De arte vitraria *or The Art of Glass* by Antonio Neri. Florentine chemist and priest, Antonio Neri traveled extensively in Italy and Holland. His writings are regarded as the most important source for the applied chemistry of the seventeenth century. They are of interest for the history of pigments, especially Book VII, which "*shows how to make yellow lacquer for painters from broom-flowers, and all other colors; with another way of making lacquer, be it green, blue, purple and all hues from every kind of plant and flower* ".

Ricette per ogni sorta di colore or *Recipes for every kind of color.* This seventeenth century codex in the library of the University of Padua contains interesting descriptions of techniques for preparing many of the colors used at that time.

Eighteenth Century

It would be impossible to list all of the many works about colors, inks and paints published in the eighteenth century. Major advances were made in printing, and new pigments and dyes, including Prussian blue, mosaic gold and Scheele's green, were discovered or synthesized through chemical research.

Nineteenth Century

With the burgeoning chemical industry, new dyes and pigments multiplied. The number of publications dealing with them is virtually infinite.

01

Minerale di cinabro (solfuro di mercurio) usato per pigmenti rossi
Cinnabar mineral (mercury sulphide) used for red pigments
用作紅顏料的朱砂（辰砂

02

Minerale di malachite (carbonati basici di rame) usato per pigmenti verdi
Malachite mineral (copper alkaline carbonates) used for green pigments
用作綠顏料的孔雀石綠 （銅鹼碳酸鹽）

03

Azzurrite (carbonato basico di rame) usato per pigmenti azzurri
Blue stone (copper alkaline carbonate) used for azure pigments
用作藍顏料的藍石 （銅鹼碳酸鹽）

04

Realgar (solfuro di arsenico) impiegato per pigmenti gialli e arancio
Realgar (arsenic sulphide) used for orange and yellow pigments
用作橙及黃顏料的雞冠石 （雄黃）

05

Lapislazzuli (silicati di alluminio, sodio e calcio) usato per pigmenti blu
Lapis lazuli (aluminium, sodium and calcium silicates)
天青石（鋁，鈉及鈣硅酸鹽）

06
Robbia (Rubia tinctorum) disegno schematico
Rubia (Rubia tinctorum) – drawing
茜草根紅顏料 (Rubia tinctorum) - 繪畫

07
Piantina di robbia
Rubia seedling
茜草根紅顏料籽生植物

08
Colorante Estratto dalla Robbia
Dyestuff Extracted from Rubia tinctorum
由 Rubia tinctorum 抽取的染料

09

Isatis tinctoria (guado cinese o tein-cheing)
Isatis tinctoria (dyer's woad o tein-cheing)
Isatis tinctoria (靛藍或 tein-cheing)

10
Piantina di Isatis indigotica
Isatis Indigotica
Isatis Indigotica

11

Disegno schematico della Indigofera pratensis
Indigofera Pratensis - drawing
Indigofera Pratensis – 繪畫

12

Piantina della Indigofera pratensis

Indigofera Pratensis

Indigofera Pratensis

13

Particolare della Indigofera pratensis
Indigofera Pratensis - detail
Indigofera Pratensis - 詳情

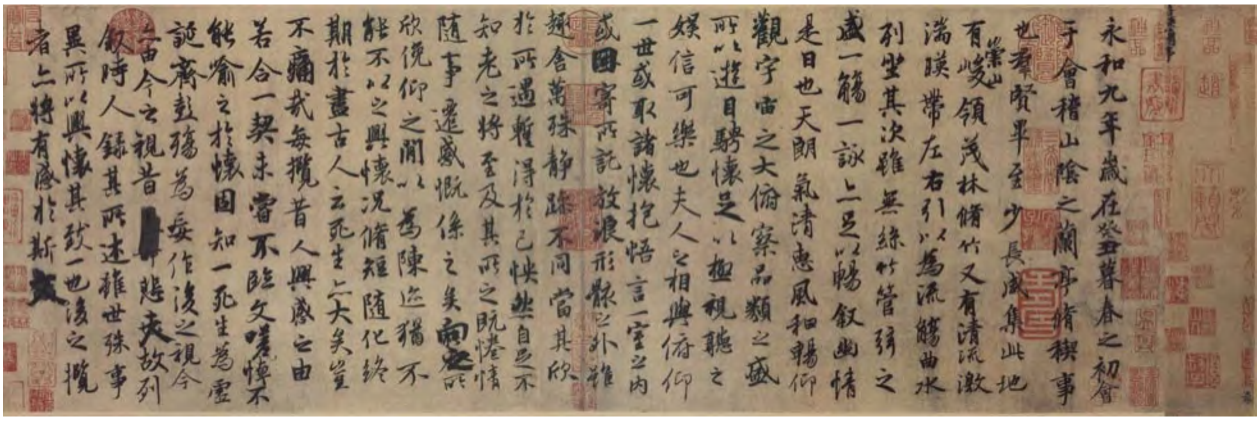
14
Disegno schematico della Reseda luteola
Reseda Luteola - drawing
木茜草 Luteola - 繪畫

15
Piantina di Reseda luteola
Reseda Luteola
木茜草 Luteola

16
Particolare della Reseda luteola
Reseda Luteola – detail
木茜草 Luteola – 詳情

17

Sistema antico per la produzione di nerofumo
Old system for the production of carbon black
碳黑的舊生產系統

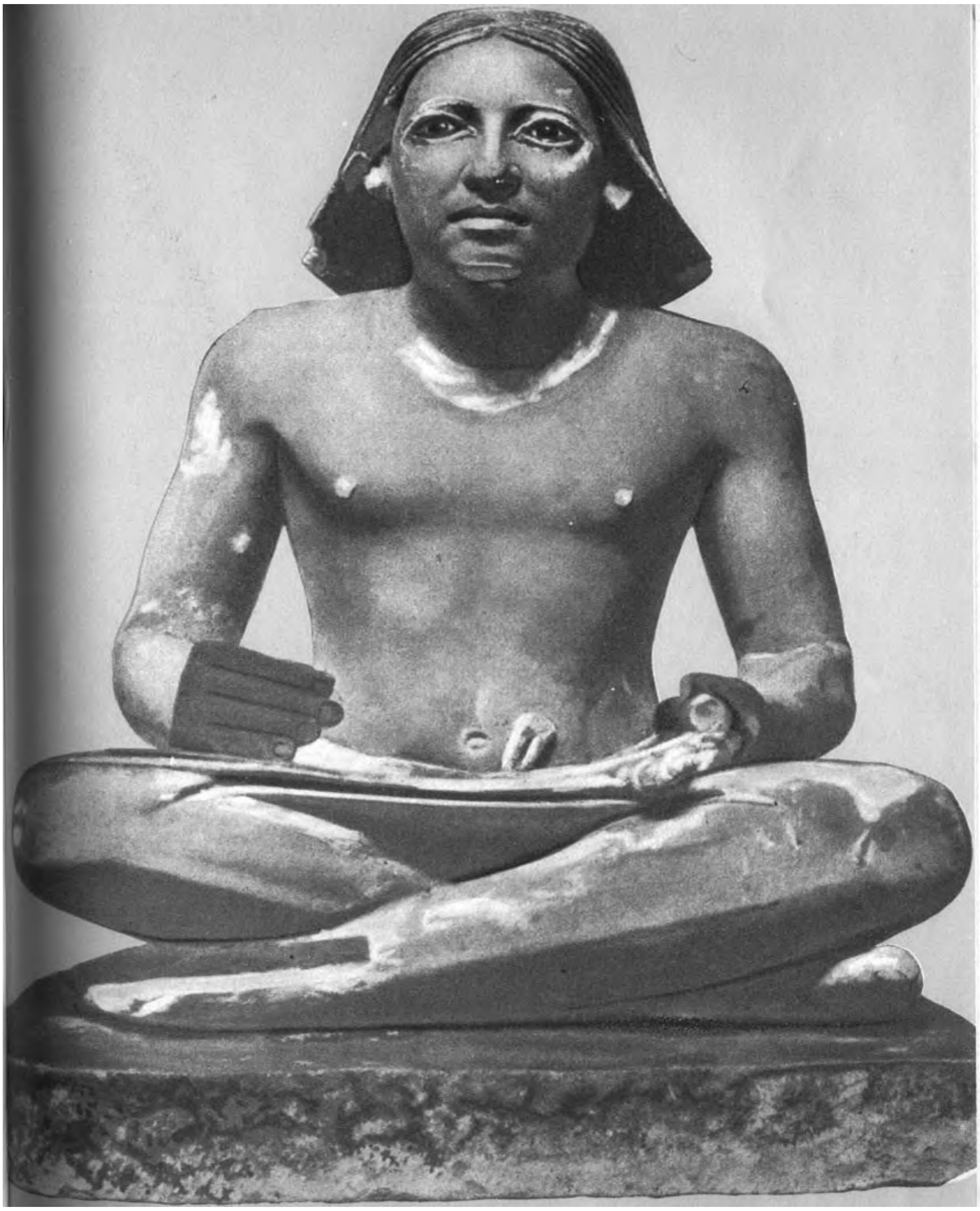


18

Scrittura esemplare cinese di LatingXu
Chinese “exemplar” writing, LatingXu
中國或「模範」書寫- 蘭亭序 LatingXu

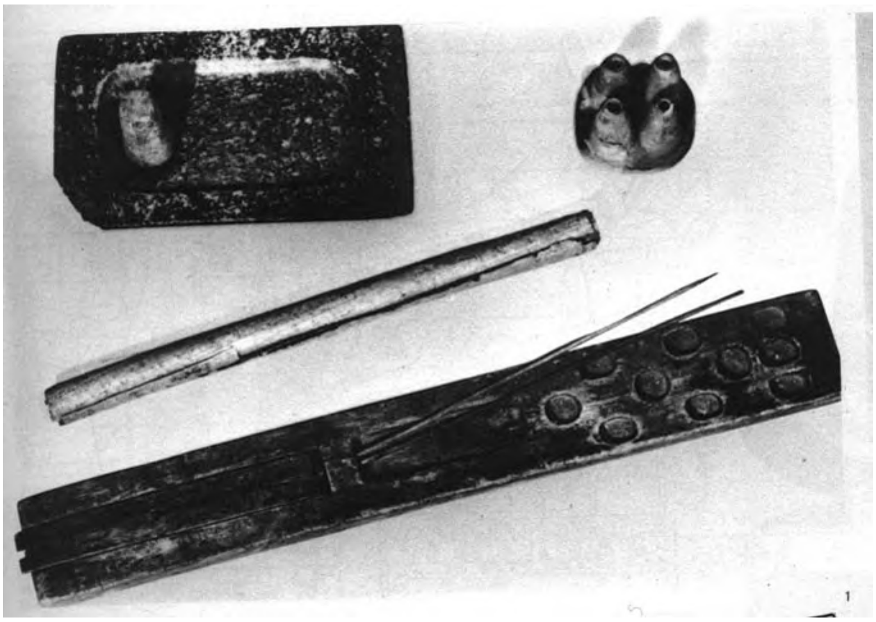
19

Pietra per macinare inchiostri di lacca cinese
Grinding stone for China lacquer inks
磨製中國墨水的石磨硯



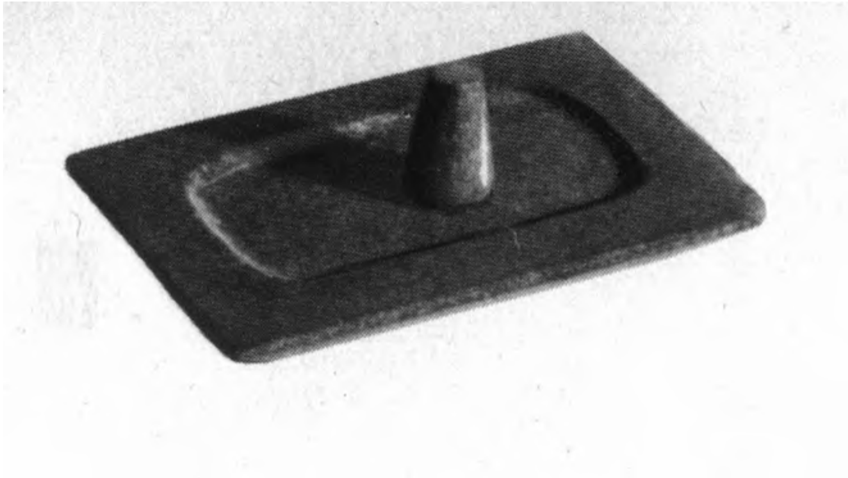
20

Scriba egizio V dinastia, proveniente da Sakkara
Egyptian scribe, 5^{th} dynasty, from Sakkara
第五朝代薩卡拉埃及抄寫員

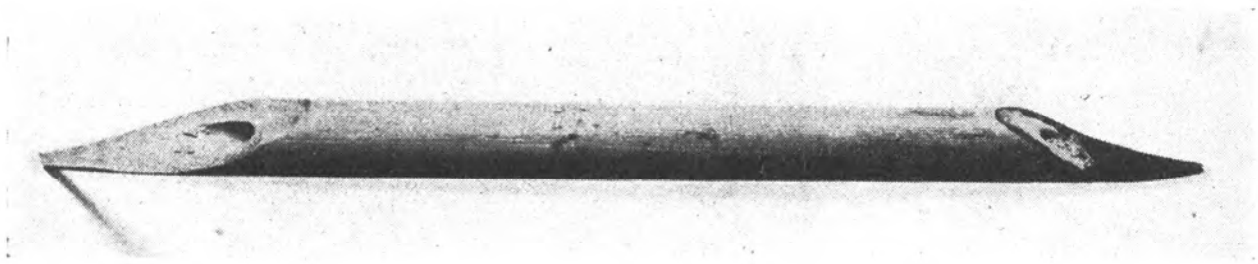


21
Attrezzatura egizia completa per scrivere
Writing set from Old Egypt
古代埃及書寫工具

22
Volumen papiraceo
Papyrus Roll (Volumen)
紙莎草紙卷（羊皮紙卷）



23
Mortaio egizio con pestello di basalto
Old Egyptian mortar with basalt pestle
古代埃及乳缽與玄武岩碾槌



24
Calamo per scrittura con inchiostri
Reed for writing with inks
墨水書寫蘆稈

25
Scuola tardo-imperiale romana, si notano i grandi rotoli
di papiro impiegati (Museo di Treviri)
Roman school of the late Imperial age where large papyrus rolls were used
(Trier Museum)
帝國末期的羅馬學院當時是用紙莎草紙卷 (Trier 博物館)

26

Amanuense romano (Klagenfurt, museo)
Roman copyist (Klagenfurt Museum)
羅馬抄寫員（克拉根福博物館）

27

Ara di T. Statilius Aper con strumenti scrittorii.
Età adrianea (117-138 D.C.), marmo, cm 189, Musei Capitolini.
T. Statilius Aper's ara with writing tools. Age of Adrian (117-138 AD), marble, 189 cm, Capitoline Museums, Rome.
T. Statilius Aper 天壇星座與書寫工具，亞德里恩時代
(117-138公元後)，大理石，189厘米，羅馬朱庇特山博物館

28

Scritta commerciale e manifesto politico pompeiani
Pompeii, commercial sign and political bill
龐貝，商業標誌及政府議案

29

Calamai romani da Pompei
Pompeii, ancient Roman inkwells
龐貝，古代羅馬墨水盛載器

30
Penna e calamaio romani
Ancient Roman pen and inkwell
古代羅馬筆及墨水盛載器

31
Rotolo del profeta Isaia trovato a Qunram
The prophet Isaiah’s scroll found in Qunram
在 Qunram 找到先知以賽亞書

32

Murex trunculus, impiegato per estrarre la porpora
MurexTrunculus from which purple is extracted
紫色被抽取自 MurexTrunculus

33

Codex Purpureus Rossanensis, del V secolo, reperito a Rossano Calabro
Codex Purpureus Rossanensis, 5th century AD, found in Rossano Calabro, Italy
在公元後五世紀意大利 Calabro 找到的 Codex Purpureus Rossanensis

34

Miniatura di Giovanni Apostolo mentre scrive l'Apocalisse (V secolo)
Miniature of the Apostle John writing the Apocalypse (5^{th} century AD)
耶穌的十二使徒之一約翰正在寫啟示錄的縮圖

35

Scriba, statua acefala di Arnolfo di Cambio (circa 1240-1302)
Headless statue of a scribe, Arnolfo di Cambio (circa 1240-1302)
抄書員的無頭雕像，阿諾爾福 （circa 1240-1302）

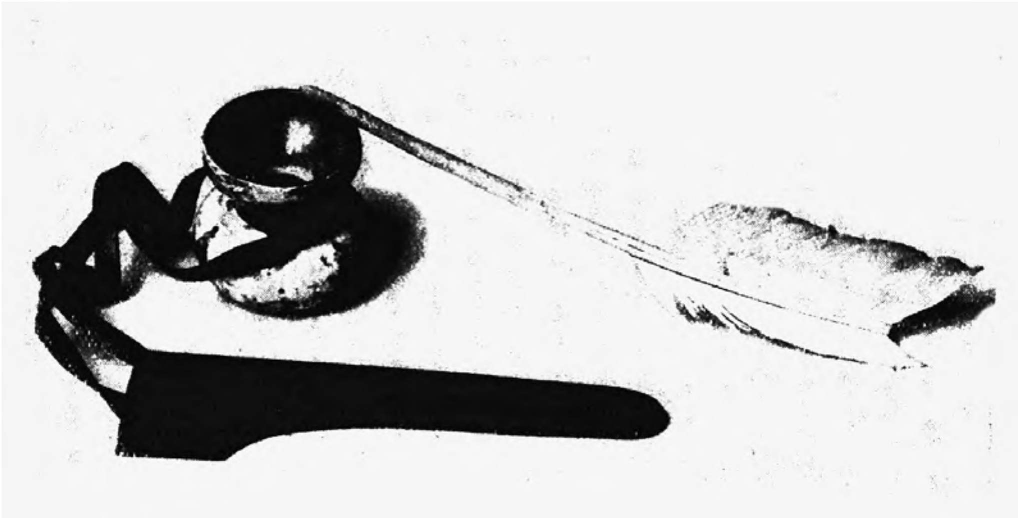
36

Materie per preparare l’inchiostro ferro gallico:
noci di galla e vasetto con vetriolo verde (solfato ferroso)
Material for the preparation of iron gall-based ink:
oak-gall and glass jar with green vitriol (iron sulphate)
製鞣酸鐵墨水的材料：櫟五倍子及綠硫酸 （鐵硫酸鹽）

37
Noci di galla su quercia
Oak-gall nuts
櫟五倍子堅果

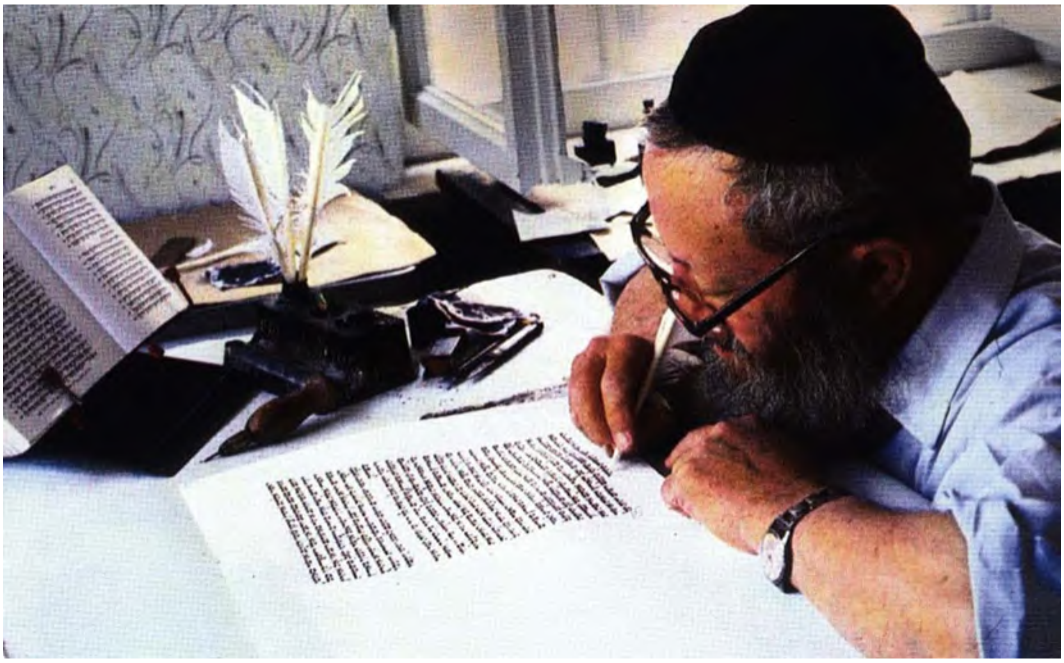
38

Art d'écrire, con inchiostro ferrogallico, dall'Encyclopédie ou Dictionnaire raisonné des sciences, des arts et des métiers, Diderot e d'Alambert, pubblicata dal 1750 al 1770
Art d'écrire, with iron gall-based ink, from the *Encyclopédie ou Dictionnaire raisonné des sciences, des arts et des métiers,* Diderot and d'Alambert, published from 1750 to 1770.
狄德羅及達蘭貝爾，由1750至1770出版



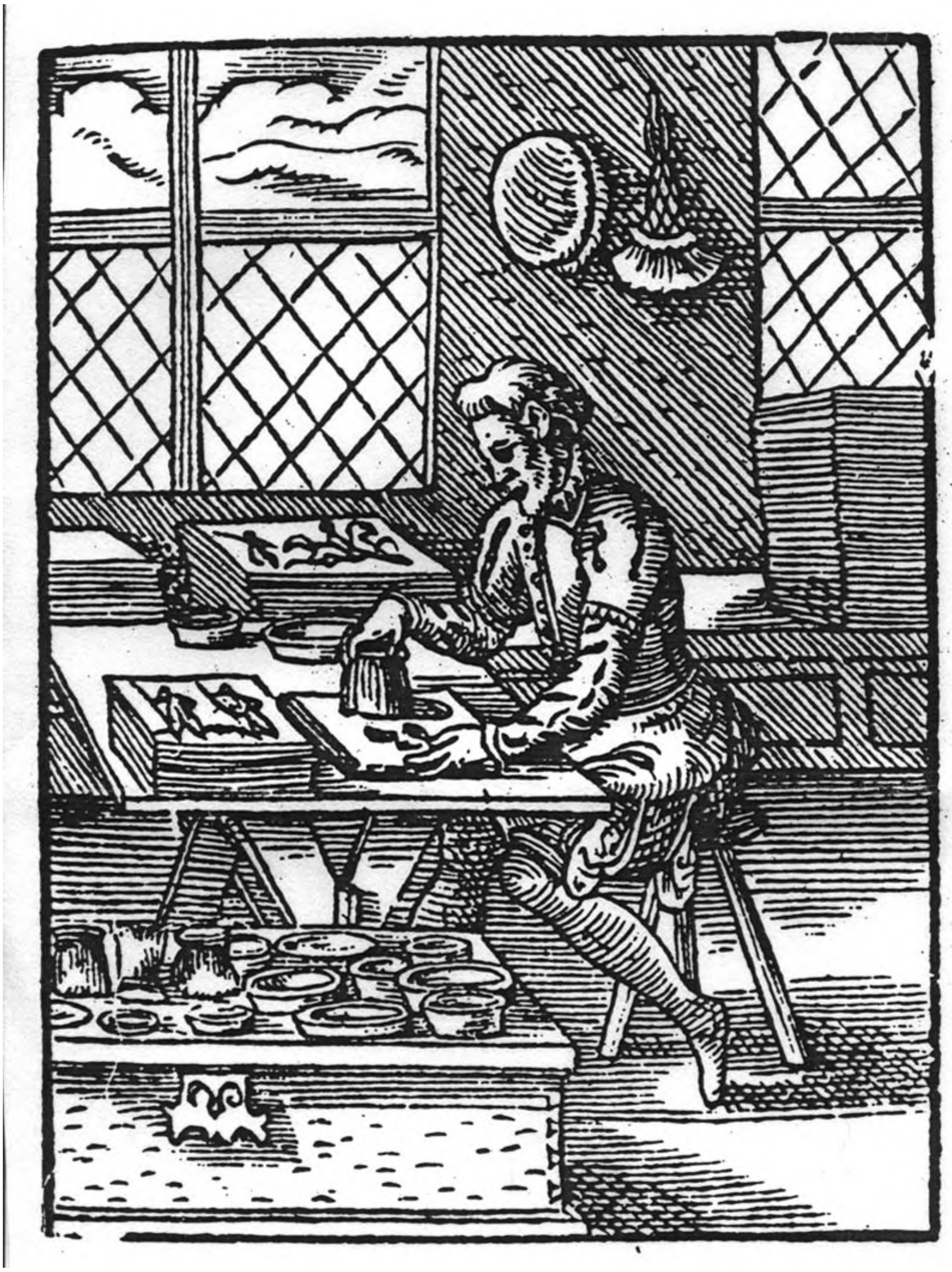
39

Calamaio settecentesco portatile, con penna e guaina
18th-century portable inkstand, with pen and case
18世紀攜帶式墨水瓶架，筆及盒



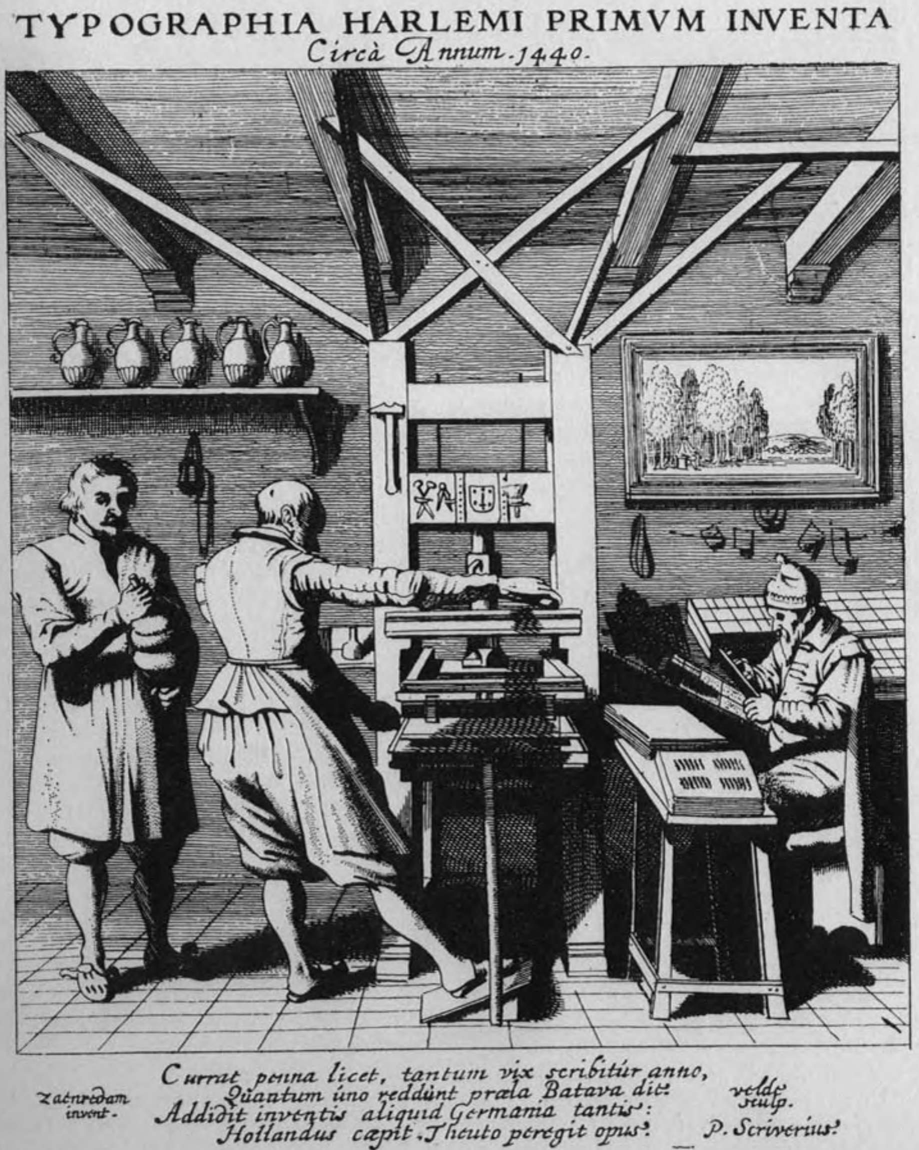
40

Moderno amanuense con penna d'oca
Modern copyist with a quill
現代抄寫員與羽毛筆



41

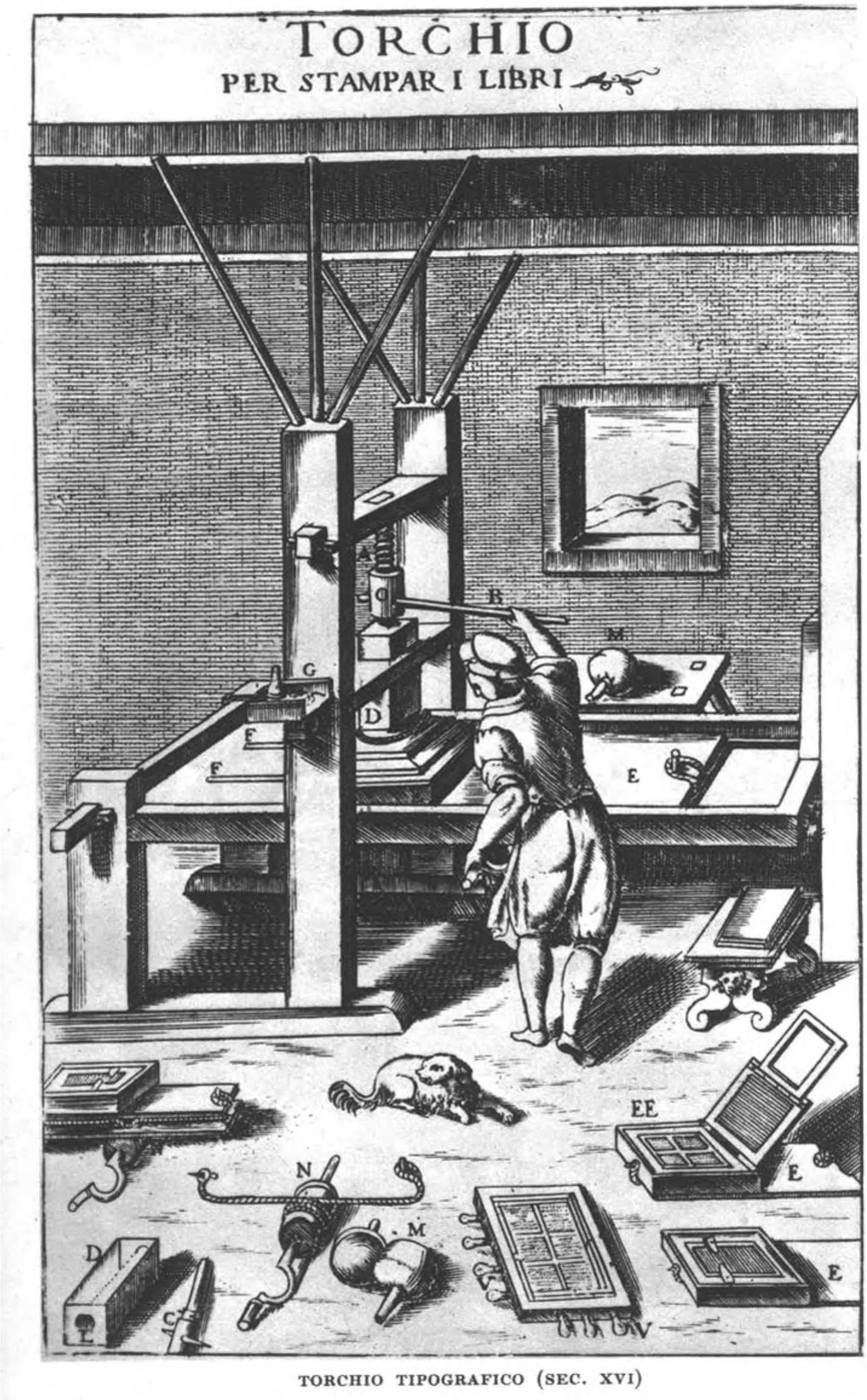
Coloritura manuale di xilografie, tipica dal Cinquecento al Settecento
Hand-colouring of xylographies, widely practiced from the 16th to the 18th century
木板水印的手作染色，廣泛應用於16至18世紀



1628. An engraving from *P. Scriverii Laure-Crans voor L. Coster van Haelem, eerste Vinder vande Boeck-Druckerey* by Pieter Schrijver, printed in Haarlem. It deals with the claims of Coster to be the inventor of printing and in the illustration here reproduced gives the first authentic and convincing representation of a press and the other equipment of a printing office. British Museum, 132.a.5.

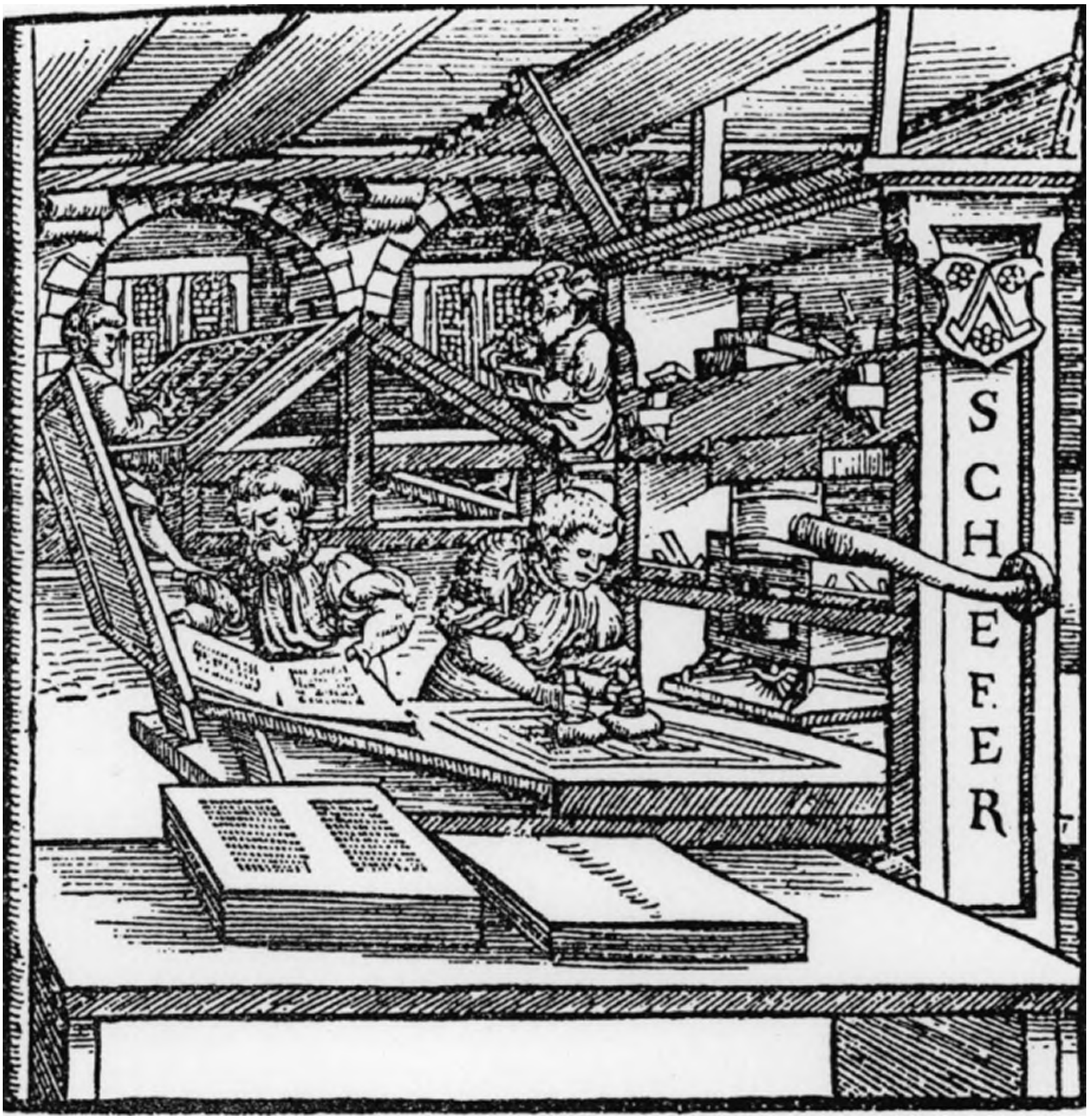
42

Prima tipografia stabilita ad Haarlem (1440),
secondo la tradizione olandese, che vuole
L. Coster inventore della composizione a caratteri mobili
Haarlem’s first-established printing works (1440); according to
the Dutch tradition L. Coster is regarded as the inventor of movable-type composition
哈勒姆第一個印刷品（1440）-根據荷蘭傳統
L. Coster 被視為可移動打字機發明者



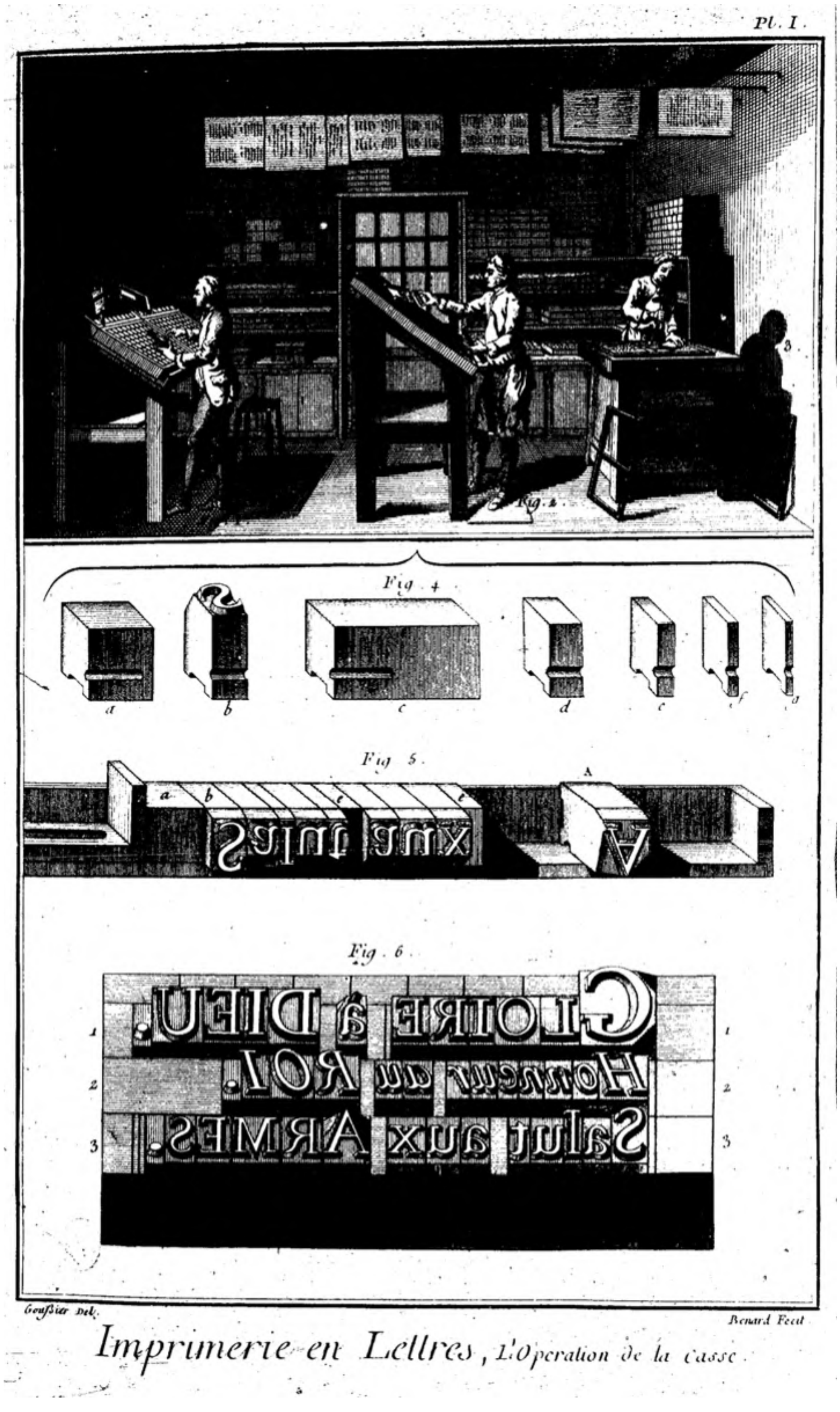
43

Torchio da stampa con evidenziati i mazzi per inchiostrare
(da V. Zonca , Novo teatro di machine et edificii, 1656)
Printing press with ink-balls and tools on show
(from V. Zonca, *Novo teatro di machine et edificii*, 1656)
附有墨珠及工具的印刷機
(V. Zonca, Novo teatro di machine et edificii, 1656)



44

Antica xilografia in cui si evidenzia il momento
di inchiostrazione della forma con i “mazzi”
Old xylography showing form inking with ink-balls
舊木版印刷法顯示墨水以墨珠形成



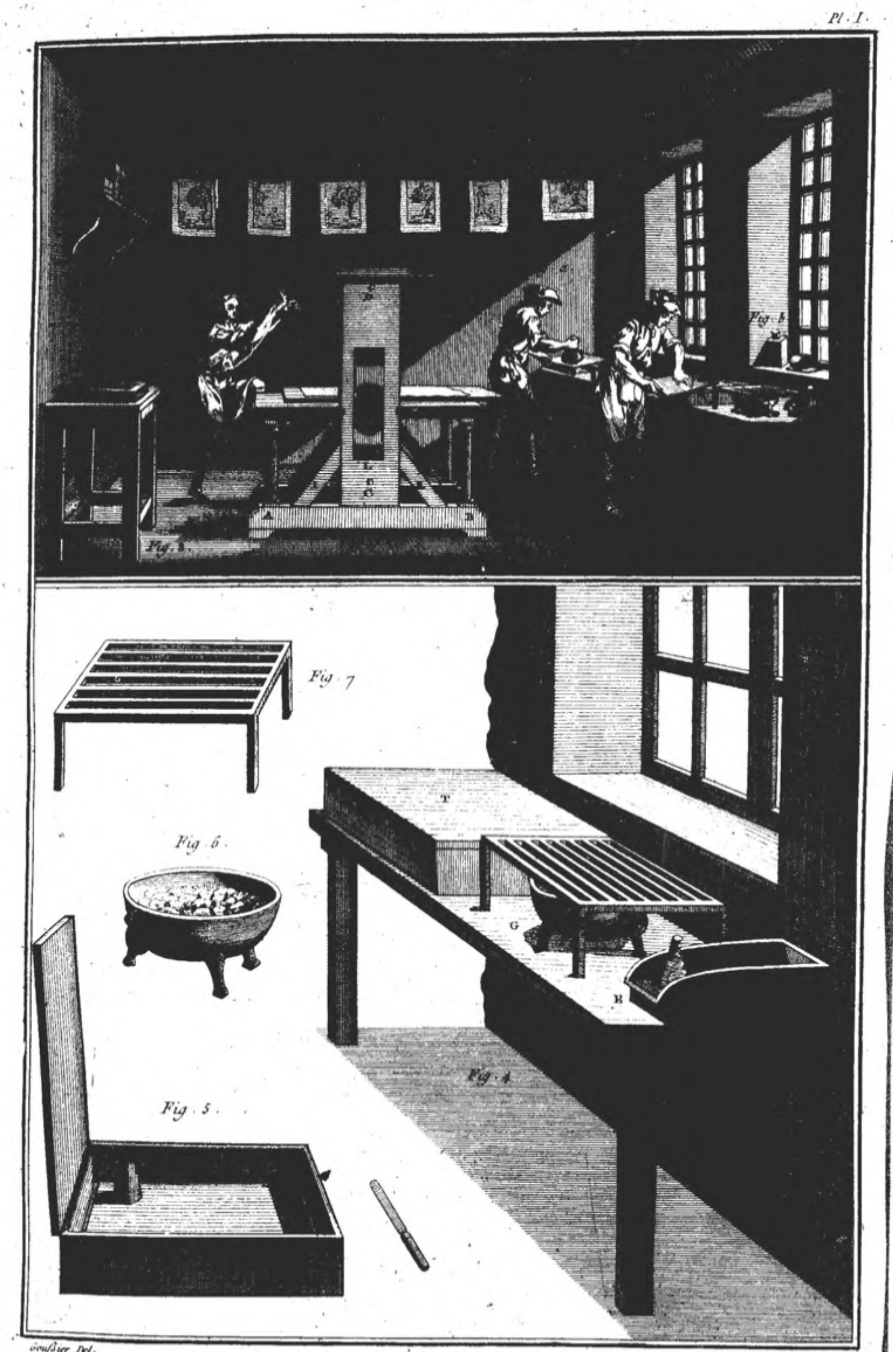
45

Encyclopédie

Composizione e stampa in Tipografia; volume 6-021

Composition and printing in printing works; volume 6-021

印刷品的組成及印刷，6-021冊



Imprimerie en Taille Douce.

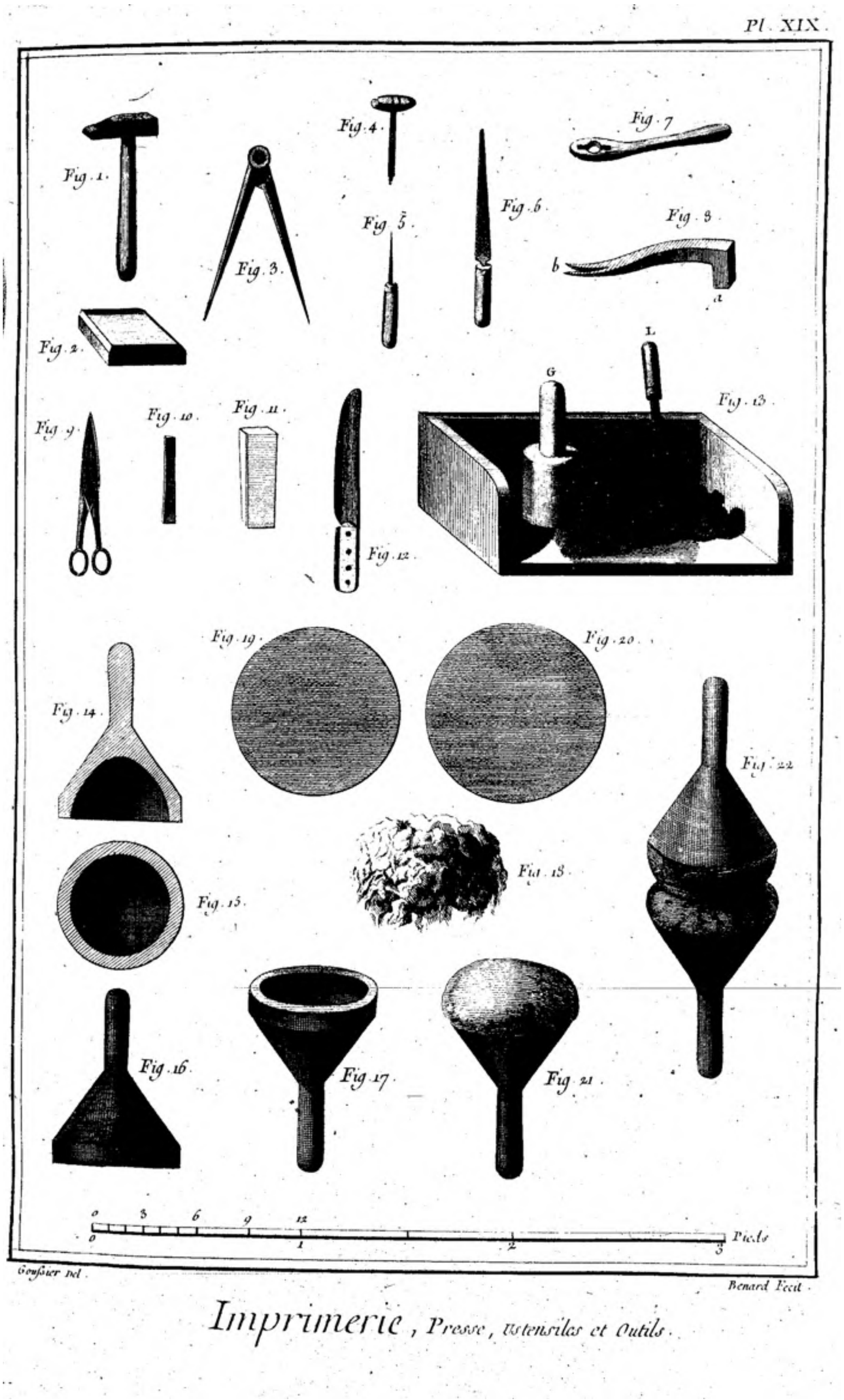
46

Encyclopédie

Stampa calcografica: torchio e attrezzature; volume 6-042

Chalcography: press and equipment; volume 6-042

銅版雕刻術：印刷機及設施，6-042冊



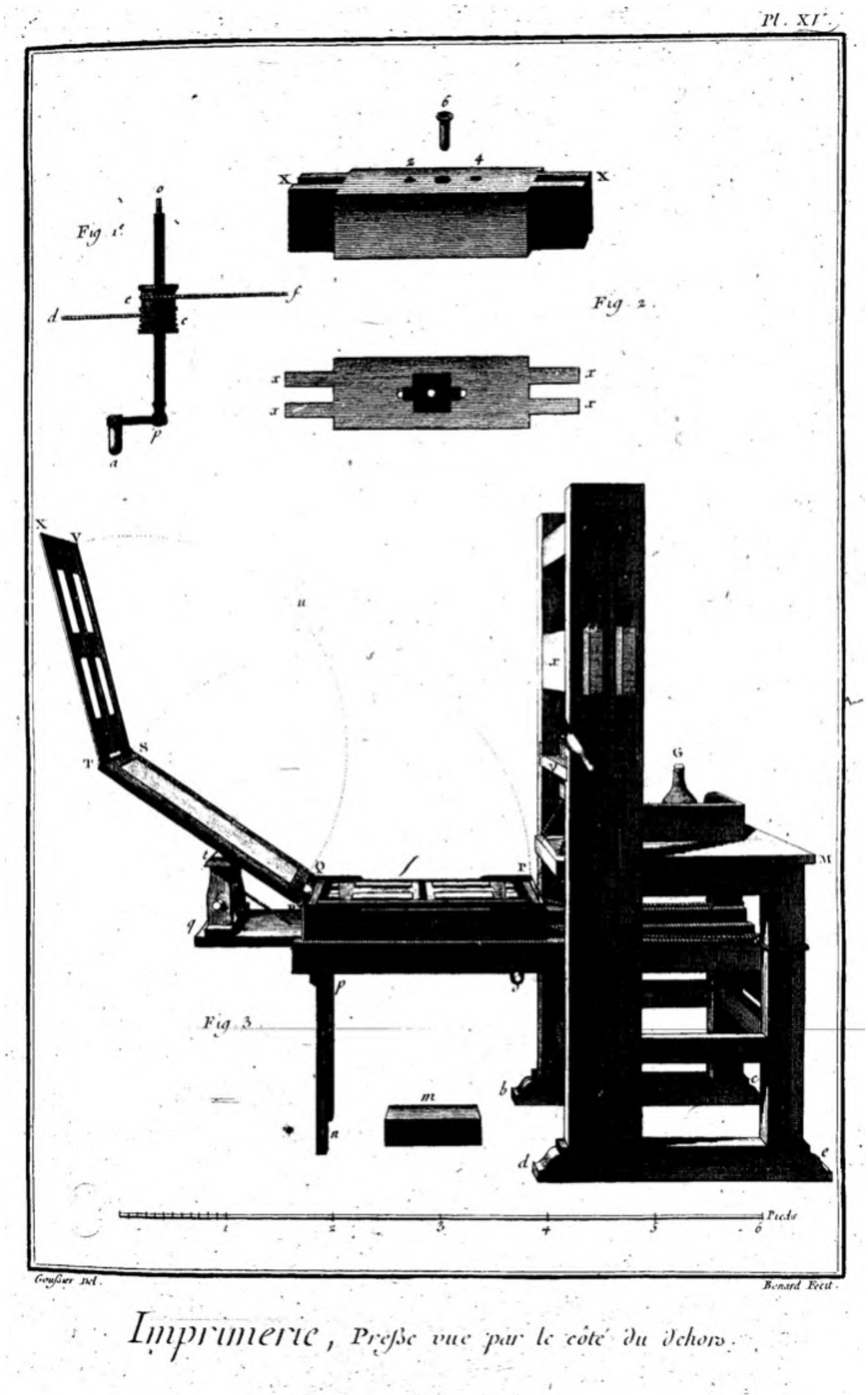
47

Encyclopédie

Utensili tipografici di vario tipo, volume 6-040

Several printing tools, volume 6-040

幾款印刷工具，6-040冊



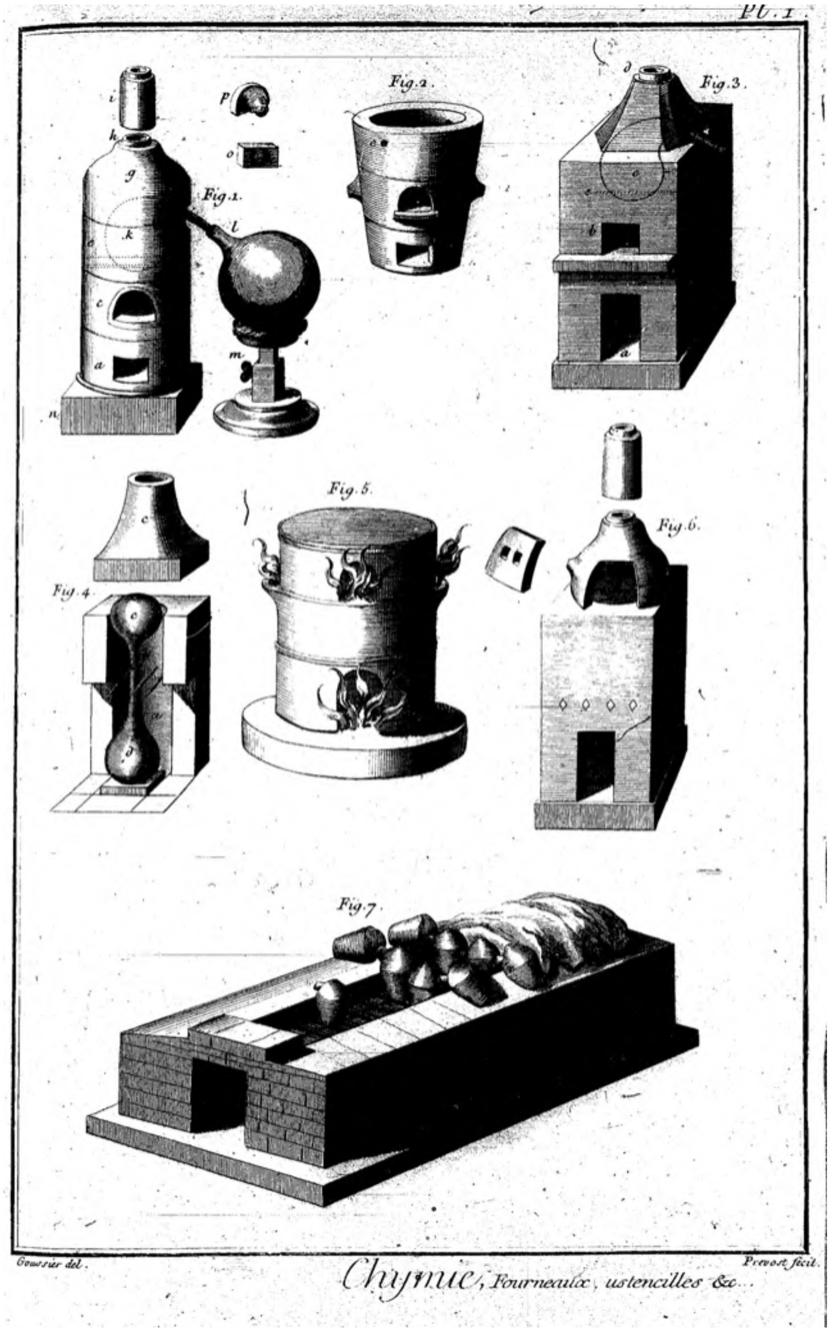
48

Encyclopédie

Torchio tipografico in dettaglio; volume 6-036

Detail of a printing press; volume 6-036

印刷機的詳情，6-036冊



49

Encyclopédie,

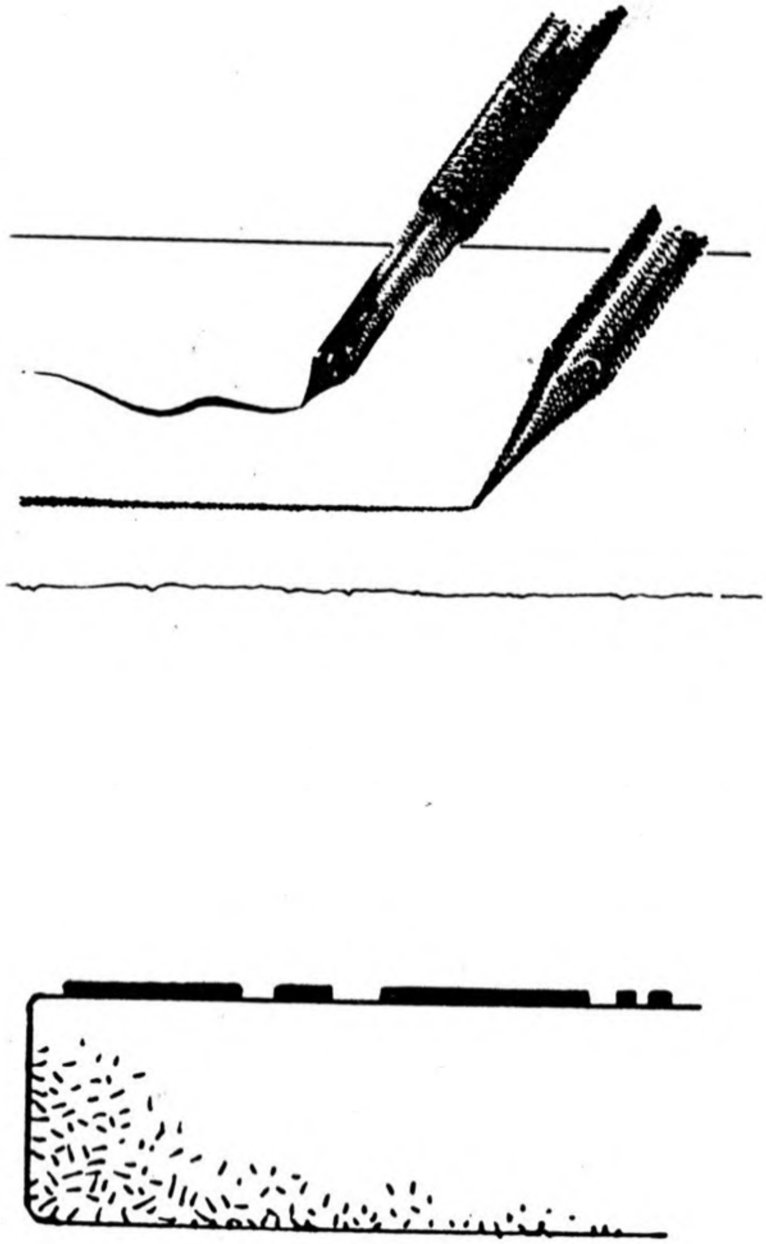
Forni e dispositivi per combustione e calcinazione; volume 2b-079

Furnaces and devices for combustion and calcination; volume 2b-079

用來燃燒及鍛燒的爐子及組件

50

Senefelder scopre le proprietà del suo inchiostro
scrivendo la lista della spesa per la lavandaia
Senefelder discovers the properties of his inks while
writing the shopping list for the laundress
塞納菲爾德在寫購物清單時發現他的墨水的特性



51

Schema di preparazione di pietre litografiche

Scheme for the preparation of lithographic stones

石版印刷石的製造方法

52

Fase di bagnatura della pietra litografica,
che precede l'inchiostrazione
Wetting of lithographic stones before inking
印刷前沾濕的石版印刷石

53

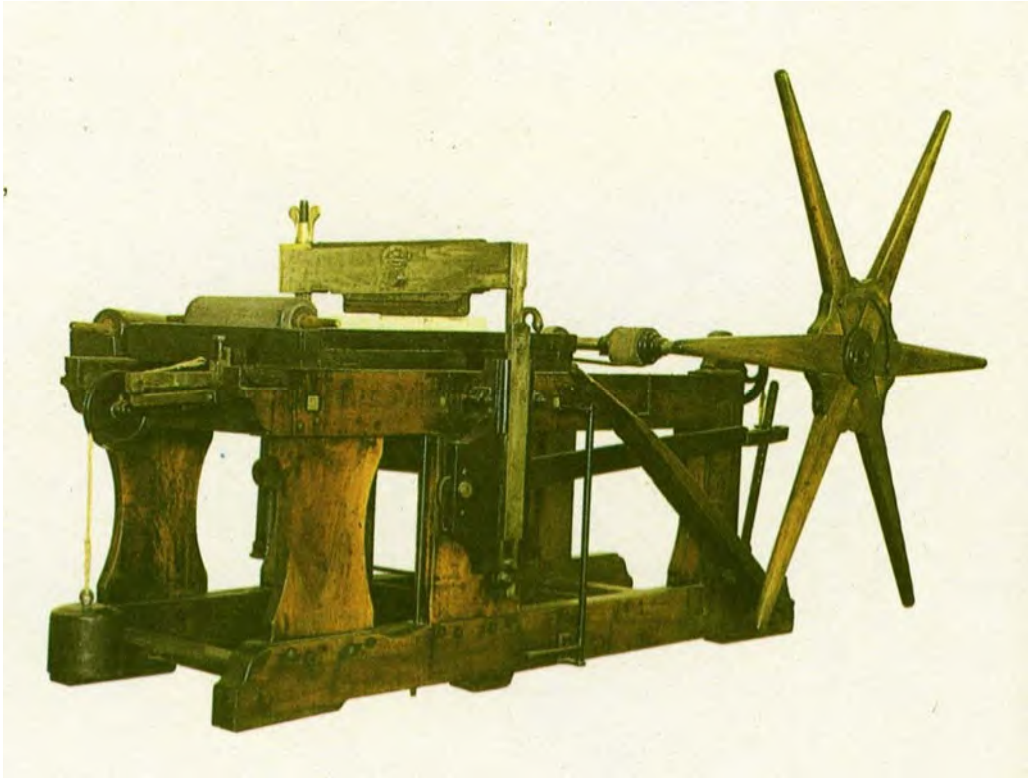
Inchiostrazione della pietra litografiche
Inking of a lithographic stone
石版印刷石沾上墨水

54

Pietra litografica con iscrizione musicale alla penna,
come le prime prodotte da Senefelder
Lithographic stone with pen-written music,
of the same kind as Senefelder’s early stones
與塞納菲爾德早期的石同樣的石版印刷與筆寫音樂

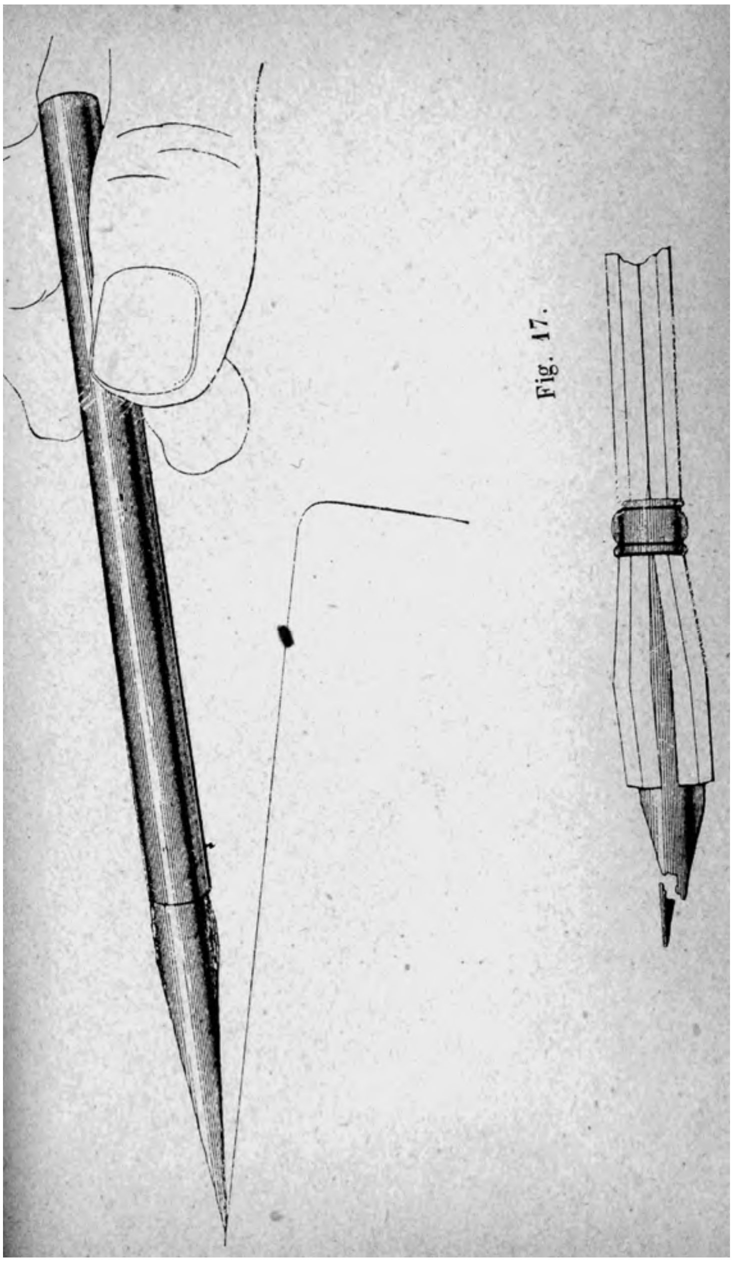
55

Pietra con iscrizione incisa alla penna,
della Società Tipografica di Padova
Stone with a pen-made inscription
for the Società Tipografica di Padova, Padua, Italy
意大利帕多瓦製作 Società Tipografica di Padova 的石與筆寫刻印文字



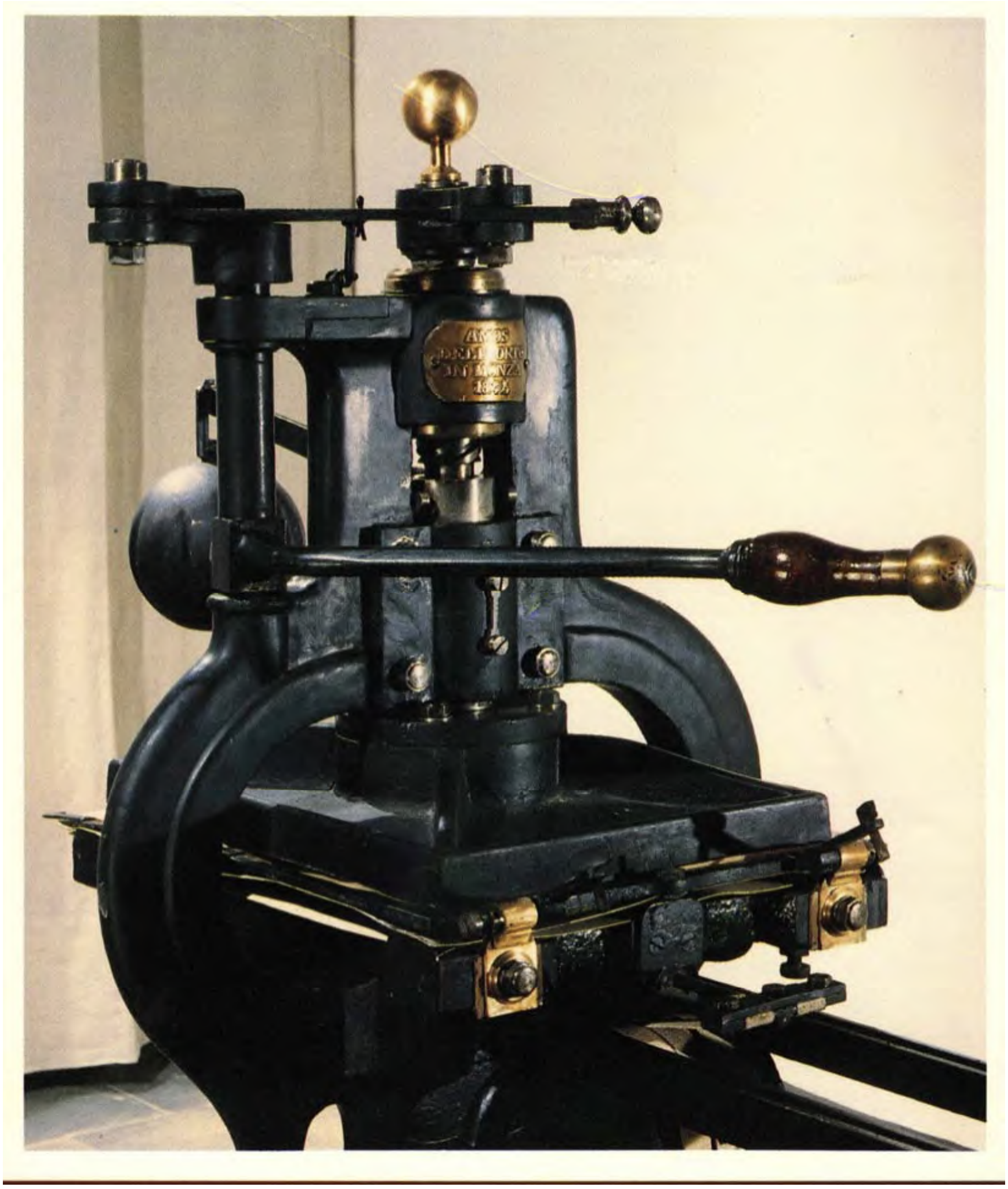
56

Torchio litografico a stella in ripresa longitudinale
Longitudinal lithographic press with star-shaped handle
附有星形手柄，縱的平版印刷機



57

Matite litografiche con portamatite
Lithographic pens with holder
平版印刷的附有支托物的筆



58

Torchio tipografico ottocentesco di fabbricazione Amos Dell'Orto, 1824
(già del Museo della Stampa dell'ing. E. Saroglia)
19th-century printing press manufactured by the company Amos Dell'Orto, 1824
(formerly the property of Eng. E. Saroglia's Museum of Printing)
19世紀由Amos Dell’Orto公司生產的印刷機，
1824（前身是Eng. E. Saroglia博物館的印刷品）

59

Pubblicità Kast & Ehinger di stile liberty, 1880
Art-Nouveau advertisement of Kast & Ehinger, 1880
Kast & Ehinger 的新藝術運動廣告，1880

60

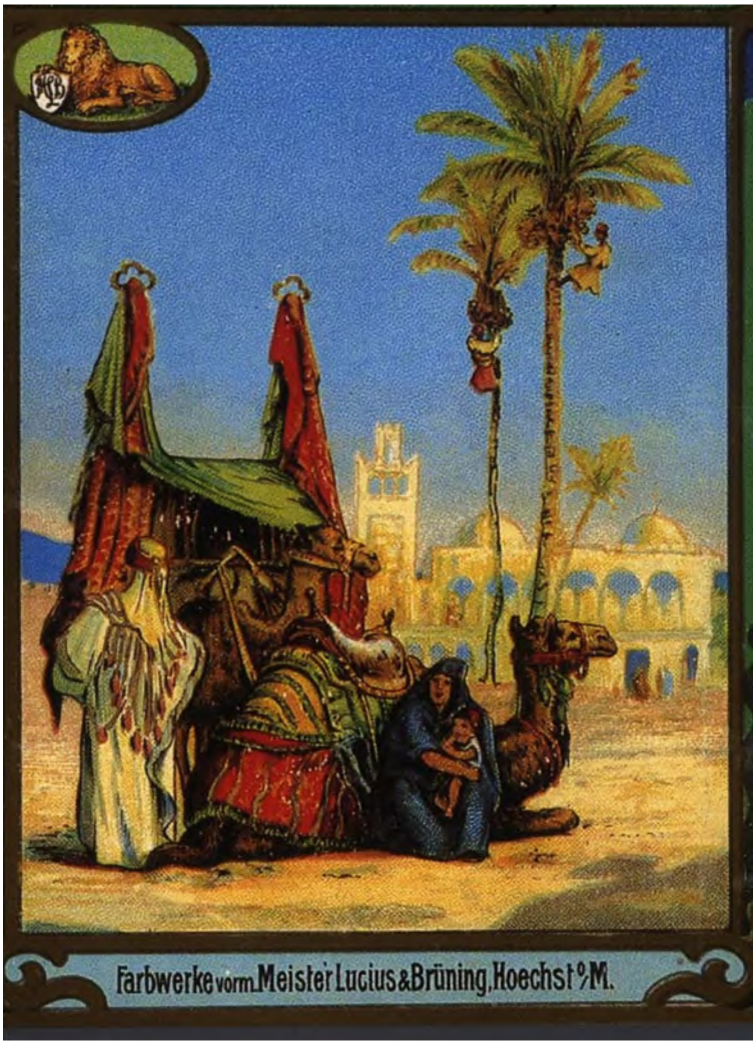
Pubblicità della nota fabbrica Lorilleux, 1884

Advertising poster of the famous printing house “Lorilleux”, 1884

著名印刷公司Lorilleux的廣告海報，1884

61

Etichetta, assai fantasiosa, del colorante magenta 1
A fanciful label of the “Magenta 1” dyestuff
一個奇異的標籤 “洋紅色1”染料



62

Farbwerke Meister Lucius & Bruning, Hoechst
Farbwerke Meister Lucius & Bruning, Hoechst, Germany
德國 Farbwerke Meister Lucius & Bruning, Hoechst

63

Manifesto dei primi del Novecento, di Antonio Rubino, per Lorilleux

Antonio Rubino, early 20th-century poster for Lorilleux

在20世紀早期為 Lorilleux 做海報的 Antonio Rubino

64

Inchiostri della fabbrica Diletti di Brisighella,
1919, Borrani, Firenze
“Diletti” inks, Brisighella, Italy,
1919, Borrani, Florence
意大利布里西蓋拉” 歡欣” 墨水 – 1919，Borrani 佛羅倫斯

65
Scatola di pennini metallici tedeschi del
primo novecento Heinze & Blanckertz
Box with “Heinze & Blanckertz” metal nibs, Germany,
early 20th century
20世紀早期德國有金屬筆尖 Heinze & Blanckertz 盒子

66
Calamaio liberty siglato WMF (1901)
Art-Nouveau inkstand with the acronym WMF, 1901
首字母縮略字WMF的新藝術運動墨水瓶架，1901

67

Curiosa etichetta della ditta Cassella di Francoforte
A curious label of the company “Cassella”, Frankfurt
法蘭克福一間公司 Cassella 一個奇怪的標籤

68

Scatole di pennini inglesi e tedeschi degli anni ‘30
English and German boxes with metal nibs, 1930’s
1930 年代英國及德國的金屬筆尖及盒

69

Cliché di zinco (fotografato specularmente) del primo
Novecento per pubblicità di un inchiostro copiativo
Early 20th-century zinc cliché (mirrored)
for the advertisement of a copying ink
20 世紀早期用作廣告抄本墨水的鋅板材 （反射）

70

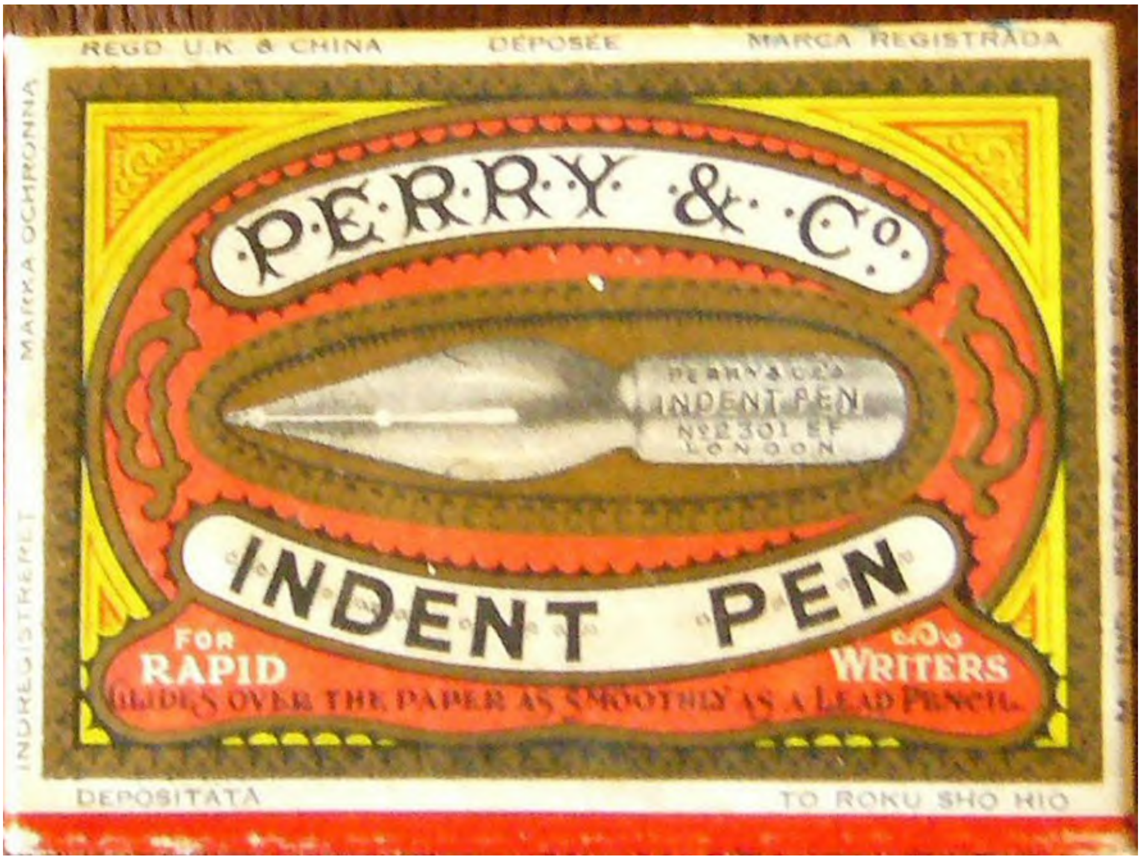
Cliché di zinco (fotografato specularmente) del primo
Novecento per pubblicità di un inchiostro per stilografiche
Early 20th-century zinc cliché (mirrored)
for the advertisement of a fountain pen ink
20 世紀早期用作廣告用的自來墨水筆的鋅板材 （反射）

71

Cliché di zinco (fotografato specularmente) del primo
Novecento per pubblicità di un inchiostro per timbri
Early 20th-century zinc cliché (mirrored)
for the advertisement of a stamp pad ink
20 世紀早期用作廣告用的印臺墨水的鋅板材 （反射）

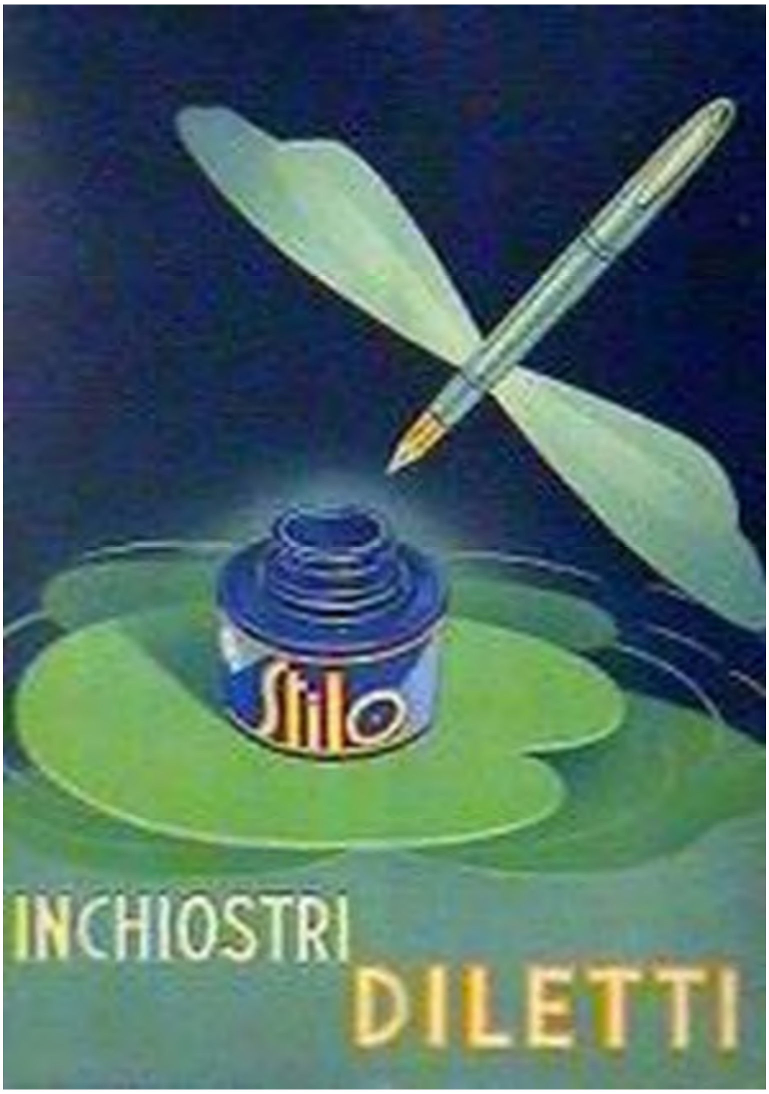
72

Pubblicità del Soluble violet della
Farbwerke Meister Hoechst con
etichetta orientaleggiante
Advertisement of the “Soluble Violet” dyestuff manufactured
by the company “Farbwerke Meister”, Hoechst, Germany, with an
Oriental-style label
德國赫司特 Farbwerke Meister 公司生產的「可溶性紫色」的廣告用上東方色彩綽號



73

Pennini inglesi Perry anni '30, "for rapid writers"
"Perry" nibs, England, 1930's, "for rapid writers"
1930 年代英國為書寫快的人而設的「柏利」鋼筆尖



74

Stilo, inchiostro della fabbrica Diletti di Brisighella, 1929
“Stilo” ink manufactured by “Diletti”, Brisighella, Italy, 1929
意大利布里西蓋拉「歡欣」公司出產的「針形樣式」墨水

75

Etichetta anonima, da “personalizzare”,
di inchiostri con amanuense orientale in primo piano
Nameless label for inks to be personalised with the manufacturer’s name and address,
showing an oriental copyist in foreground
無名標籤墨水被工廠名字或地址命名，顯示出模仿者重要的地位

76

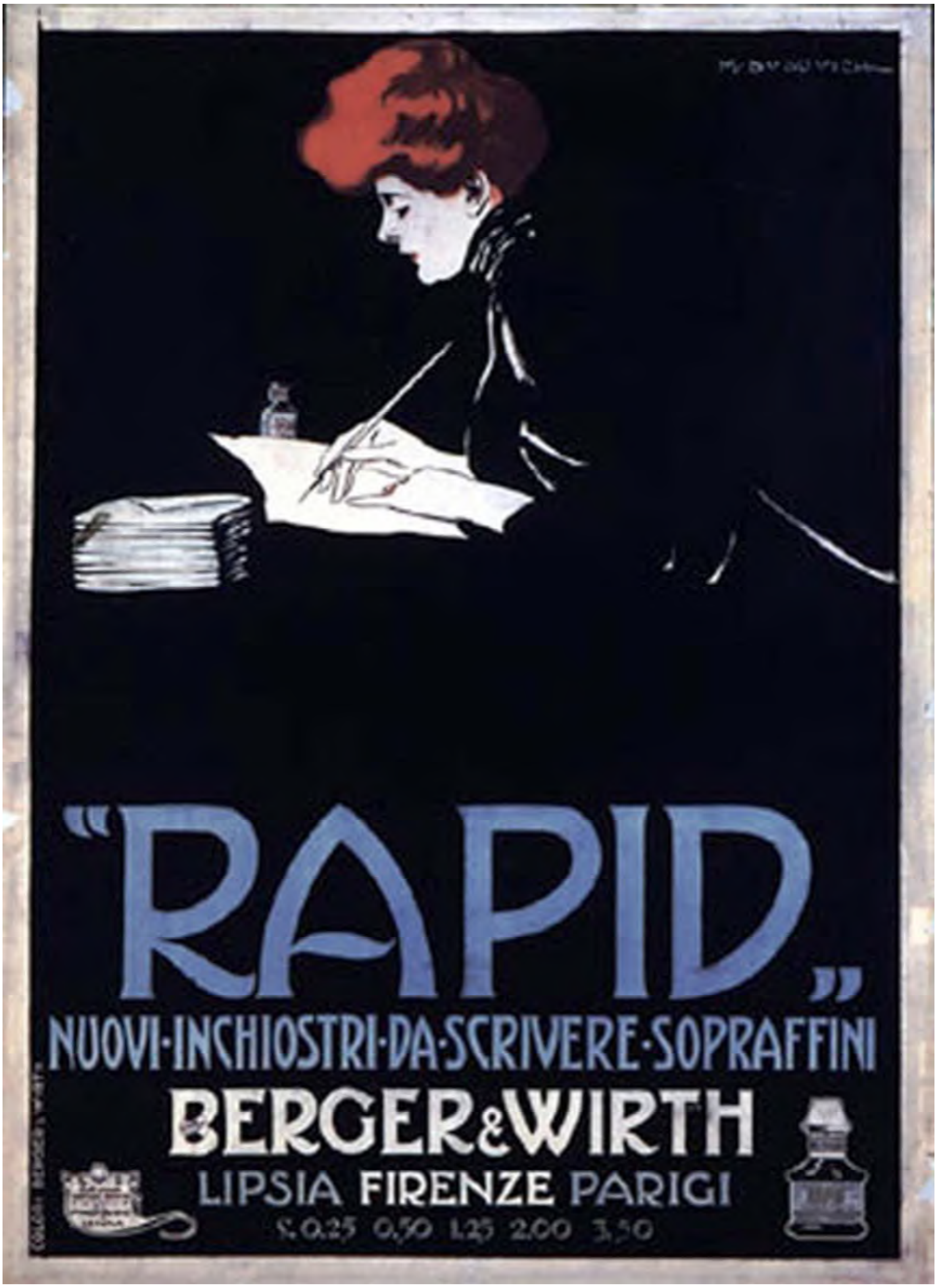
Offset inks, di illustratore anonimo
(forse Depero), ditta Sadolin e Holmblad
“Offset inks” label, author unknown
(possibly Depero), Sadolin and Holmblad
平版印刷墨水標籤，無名氏 （很可能是Depero）Sadolin 與 Holmblad

77

Combinazione ed armonia di colori, libretto tecnico del 1919 per tipografi

Combinazione ed armonia di colori (Combination and Harmony of Colours), technical manual for printers, 1919

（顏色的組合及和諧）1919 年印刷工的手動技術



78

Marcello Dudovich, Rapid, nuovi inchiostri da scrivere sopraffini, Berger e Wirth, Firenze

Marcello Dudovich, *Rapid*, *the newest top-class writing inks*, Berger e Wirth, Florence

佛羅倫斯 Berger e Wirth 的Marcello Dudovich，快速，最新頂級書寫墨水

79

Colorante “Prima Roseine” della ditta
Cassella di Francoforte, con etichetta orientaleggiante
“Prima Roseine” dyestuff manufactured by the company “Cassella”, Frankfurt,
with an Oriental-style label
由法蘭克福Cassella公司生產的「Prima Roseine」染料用上東方色彩標籤

80

Curioso pennino denominato “penna reale”,
che porta inciso lo stemma sabaudo, 1908
An odd nib named “Penna Reale” (Royal Pen)
with an engraving of the Savoy coat of arms
叫 Penna Reale （皇室筆） 舊鋼筆尖附有一層皺葉甘藍的筆桿

81
Pennini per tiralinee anni '40
Drawing pen nibs, 1940's
1940 年代繪畫用的筆尖

82
Raccolta di pennini metallici di varie marche, anni '50
A collection of metal nibs of different manufacturers, 1950's
1950 年代不同生產商的金屬筆尖系列

83

Colorante Orange della fabbrica Hoeschst, venduto a La Paz
“Orange” dyestuff manufactured by the company “Hoeschst” on sale in La Paz, Bolivia
由玻利維亞共和國拉巴斯 Hoeschst 公司生產的橙色染料

84

Cuscinetto per timbri "Patriottico" anni '30
Stamp pad "Patriottico", 1930's
1930 年代圖章印色盒 Patriottico

85

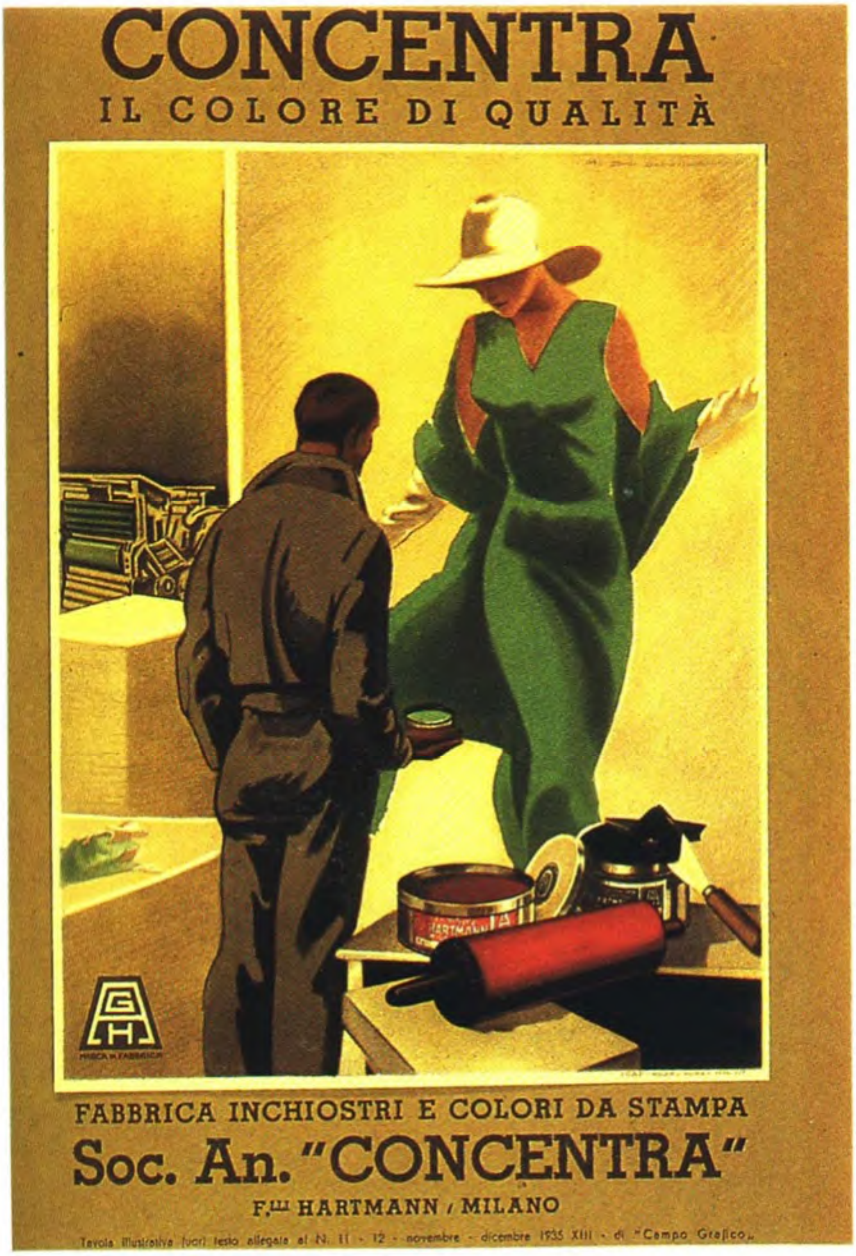
Inchiostri Serie Impero, Concentra, Milano, 1936

Inks of the “Impero” series, Concentra, Milan, 1936

1936 年米蘭 Concentra， Impero 系列墨水

86

Pennini “Nazionali” Presbitero
“Nazionali” nibs, Presbitero
Presbitero，Nazionali 鋼筆尖



87

Inchiostri e colori della soc. an. Concentra, Hartmann, Milano
Inks and colours manufactured by “Concentra”, Hartmann, Milan
米蘭 Hartmann 的 Concentra 生產墨水及顏色

88

Scrittura “Imperiale”, da un manuale di calligrafia del 1939
“Imperiale” calligraphy style from a calligraphy handbook, 1939
來自 1939 年書法手冊的 Imperiale 書法風格

89

Inchiostri e colori Etelia, Firenze, 1927

Inks and colours manufactured by “Etelia”, Florence, 1927

佛羅倫斯 Etelia 生產的墨水及顏色

90

Inchiostro Minerva, blu-nero, Casale Monferrato
“Minerva” black-blue ink, Casale Monferrato, Italy
意大利 Casale Monferrato 的 Minerva 藍黑色墨水

91

Inchiostro stilografico blu-nero Mercurius
della torinese Gnocchi
“Mercurius” black-blue fountain pen ink manufactured by Gnocchi, Turin
都靈 Gnocchi 生產的 Mercurius 黑藍色自來墨水筆

92

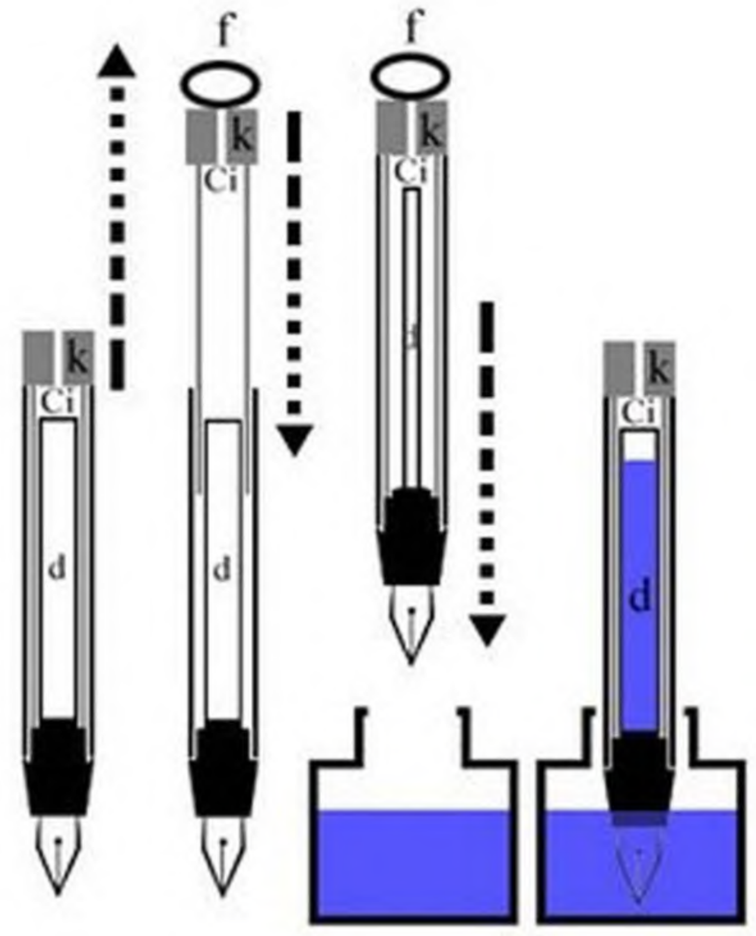
Inchiostro stilografico G.M. Lampo blue, Firenze, anni ‘40
“Lampo” blue fountain pen ink, Florence, 1940’s
1940 年佛羅倫斯生產的 Lampo 藍色自來墨水筆

93

Manifesto anonimo del 1953 per la penna Ancora
Advertising poster of the “Ancora” pen, 1953
1953 年 Ancora 筆的廣告海報

94

Inchiostro blu-nero a base tannica della ditta Gnocchi
Tannic blue-black ink manufactured by “Gnocchi”
Gnocchi 生產的單寧藍黑色



95

Sistema carica per penna stilografica
Fountain pen refilling system
自來墨水筆加墨系統

96
La mitica stilografica “Aurora 88”, anni ‘50
The legendary fountain pen “Aurora 88”, 1950’s
1950 年代著名的自來墨水筆 Aurora 88

97

Boccette di inchiostri stilografici degli anni ’60
Fountain pen ink bottles, 1960’s
1960 年代自來墨水筆墨水瓶

98

La notissima penna per disegno tecnico Rotring
The famous “Rotring” pen for technical drawing
著名的技術性繪畫用的 Rotring 筆

99

Serie di boccette di inchiostri di china colorati. Pelikan, Anni ’60
China drawing ink bottles, “Pelikan”, 1960’s
1960 年代中國繪畫墨水瓶 Pelikan

100

Penne a sfera Sferon della Fila
“Sferon” ball pens manufactured by “Fila”
Fila 生產的 Sferon 圓珠筆

101

Penne a sfera senza refill Stiletta
“Stiletta”, refill-less ball point pens
Stiletta 少替換筆芯圓珠筆

102

Refill per penne gel ed inchiostri della Reinol (Borgaro Torinese)
Gel pen refills and inks manufactured by “Reinol”, Borgaro Torinese, Italy
意大利 Borgaro Torinese， 雷諾生產的中性筆筆芯及墨水

103

Pubblicità del Colorificio Italiano anni '70
Advertisement of the “Colorificio Italiano”, 1970’s
1970 年代 Colorificio Italiano 的廣告

104

Manifesto per la ICI del noto grafico Armando Testa
Advertising poster for “ICI” by the famous Italian art designer Armando Testa
由意大利名設計師 Armando Testa　設計的 ICI 廣告海佈

105

"Inchiostri profumati" della Reinol (Borgaro Torinese)

Advertising poster of the scented inks manufactured by "Reinol", Borgaro Torinese, Italy

意大利 Borgaro Torinese ， 雷諾生產有氣味墨水廣告海佈