INK MANUFACTURE

INK MANUFACTURE

INCLUDING

WRITING, COPYING, LITHOGRAPHIC, MARKING, STAMPING, TYPEWRITER AND LAUNDRY INKS

BY

SIGMUND LEHNER

REVISED AND COMPARED WITH THE SEVENTH GERMAN EDITION

BY

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CANTOR LECTURER ON INKS

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PREFATORY NOTE.

THE principle I have followed in revising the third edition of this well-known practical handbook has been to make only such alterations as were necessary to bring the chemical statements in the German text into line with modern views. As the author claims that he has personally tested every recipe, I have not altered their manufacturing details but have made a few additions to their number. Where I differ from the author on some practical questions I have also made no change, since the book is intended to be a record of his experience, not mine.

The new matter added to this edition has increased the number of pages from 171 to 212, and separate chapters have been given to several subjects, such as typewriter inks, which were not so fully dealt with in the last edition.

C. AINSWORTH MITCHELL.

June, 1926.

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1.

INTRODUCTION.

SINCE human progress reached the stage of written communication of ideas, there has been a constant endeavour to simplify writing materials, just as the tendency to simplify the forms of ideographic symbols has developed into the important art of writing.

The Assyrians wrote cuneiform inscriptions on tablets of clay, and the Egyptians chiselled hieroglyphics on granite, or painted them with the brush on the walls of their tombs and temples. The first impulse towards the general practice of writing, however, came with the invention of papyrus, which stands in close relationship to paper. Modern writing material indeed derives its name from the word *papyrus*. Very many papyrus-rolls have come down to us from the ancient Egyptians, and these show that very many were able to write, especially as the papyri include memoranda of comparatively small importance, such as cookery recipes.

Long after the Chinese and Japanese had learnt the art of writing on material resembling the modern paper with a brush, the Greeks and Romans used tablets covered with wax, on which they wrote with a pointed stylus.

And yet writing inks were known to them, for Pliny, Vitruvius, and other classical authors mention them, and Dioscorides gives a special recipe for making ink. The ink of the Greeks and Romans was practically the same as that of the Chinese, and consisted mainly of fine lampblack distributed in a suitable fluid medium. Similar substances are used as the principal pigments in the black printing ink of to-day

The German word for ink (*Tinte*) comes through *tinge*, from the Latin *tingere*, to dye or to colour.* Thus an ink means a liquid that will produce a permanent colour.

Old deeds and other parchments show us that even in the early Middle Ages the art of ink making had been brought to a relatively high degree of perfection. In fact, written characters 800 years old are often still quite black, whereas those of a much more recent date have faded to a faint yellow. When we see a MS. which has become almost illegible in fifty years or less, we are inclined to think that the knowledge of ink manufacture has gone backwards instead of forwards. We must not forget, however, that the durability of an ink depends not merely on itself, but also on the substance it is written on. Many of the substances now used in preparing papers, such as lime and chlorine, have, even when present in very small quantities, a destructive effect upon an ink which if used on pure parchment would last as long as some of the monastic productions of the Middle Ages have done. Much of our bleached papers contains chlorine, which sooner or later destroys the paper. It is thus useless to write documents intended for long preservation with indelible ink if such paper is used to write them on. Modern books printed upon paper that has been bleached with chlorine will disappear in a few centuries by the disintegration of the paper. This defect attaches particularly to the paper made from wood pulp, which is now widely used on account of its cheapness.

* The English word *ink* is derived, through the old French *enque*, from the Latin *encaustum* (Greek, *eghauston*), originally indicating coloured clay burnt into tiles. Subsequently the term *encaustum* was applied to the purple ink used by the Roman Emperors.

This in a few years turns brown, and becomes so brittle that it breaks when folded. Printing ink, on the other hand, which has carbon as its black pigment, is practically imperishable. The disadvantages of such paper are now realised, and important books are printed on paper which contains no trace of free chlorine. The durability of unbleached vegetable fibre is well shown by the linen wrappings of the Egyptian mummies. Woven 4000 years ago, some of these fabrics are now scarcely brown, and are still fairly strong. The characters and designs on these mummy cloths are still quite distinct.

The manufacture of ink was carried on empirically and on quite a small scale until a comparatively late period. One of the first to apply scientific methods to the manufacture was Lewis, at the end of the eighteenth century. Then, in the early part of the nineteenth century, came Berzelius and Böttger, to mention only two of those who contributed to our technical and scientific knowledge of the subject, and since then there have been numerous chemical investigations of the nature of inks and their constituents.

The modern methods of manufacturing ink have been influenced by alterations in other writing materials. One of these is the substitution of smooth white machine-made paper for the grey or brown hand-made paper. For the manufacture of this sized paper the raw material has to be strongly bleached, with the result that it almost invariably contains chlorine or lime. It has thus become important to find inks that will resist the slow action of these substances. This may appear a very simple matter, but is in reality a difficult one. The second factor is the substitution of the steel pen for the quill. Whilst in former times the goose-quill only was used for writing and the raven-quill for drawing, the steel nib is now almost universally employed for both. The substance of a quill is extremely resistant to chemical action. Steel, on the other hand, is readily corroded by very many things. Even very dilute acid in the ink will soon make a nib unusable. Acid-free inks have therefore been invented which will not act on iron, and many attempts have been made to devise a protective coating for the nib, by covering it with copper, silver, or even gold. This coating, however, soon gets worn off the tip of the nib, even in using the smoothest paper ; and for this reason fountain pens are now provided with nibs of gold alloy, the tips of which are hardened with iridium.

In view of the numerous requirements to which an ink has to answer, it is obvious that the manufacture requires both technical skill and scientific knowledge, and although some of the chemical reactions involved in the manufacturing processes are still not quite clear, yet sufficient is now known of their course to prevent the ink maker from working in the dark.

II.

VARIETIES OF INK.

By ink in general we understand a black or coloured liquid intended to make durable signs on any surface.

Inks may be classified according to their uses into several fairly definite groups, as follows :—

Writing Inks, for writing with a pen ; closely allied to these are the *Copying Inks*, also for use with a pen, but from which impressions can be reproduced. One variety of copying ink is *Hektograph Ink*, which allows many copies to be made from an original written upon a specially prepared ground.

Ink Powders are powders which produce ink by mere solution in water.

Ink Pencils are closely allied to these. On slightly damp paper they make marks resembling those made with aniline inks.

Drawing Inks are intended for the production, by means of an ordinary pen or a drawing pen, of drawings in a black medium suitable for photographic reproduction.

Lithographic Inks are used solely for writing and drawing on lithographic stone, and these must resist the corrosive fluids used by lithographers.

Marking Inks are used as a substitute for the old practice of embroidering names or initials on garments ; the characters made with them and suitably treated should not be removed when the fabric is washed with soap and water.

Printing Pigments include those used for marking guiding lines for embroidery, as well as those for india-rubber stamps, although the latter differs somewhat from most of the others. To printing pigments, in the wider sense of the word, belong also the compositions used for typewriter and tape-machine ribbons; as also for the "carbon" papers for duplicating work. Many of them permit of copies being taken, so that they are closely connected with the copying inks.

Among ink specialities are included gold, silver, and "sympathetic" inks, and every ink maker ought to know how to make these varieties, although they are not much in demand.

The number of inks and allied products is considerable. In the following pages, therefore, only those formulæ that have been tested will be given, and no mention will be made of others, some of which appear to have been drawn up haphazard.

Most inks (or rather writing inks) are chemical products in the fullest meaning of the word, i.e. chemical reactions take place in their production, resulting in the formation of new, pigment-yielding compounds. Thus, by bringing together solutions of copperas (iron sulphate) and gallo-tannin, a black precipitate, which was the fundamental constituent of the older type of inks, is produced; this phenomenon, of course, is one of the longest known chemical reactions. The study of the processes underlying the formation of inks has been developed into a special branch of chemistry, the special object of which is to discover how to produce permanent and ineffaceable writing. It is unnecessary to lay stress upon the importance of this aim, although unfortunately it has still not been unquestionably attained, and, indeed, is hardly likely to be.

The old method of making ink, which has continued down to the present day, consisted in mixing solutions of gallotannin and of iron compounds; hence the reactions involved and the conditions necessary for the production of a serviceable ink in this way have been specially studied. Commissions, which included some of the most distinguished chemists of the last century, investigated the subject; even Berzelius invented a new ink—vanadium ink—which, however, did not altogether come up to the expectations as to its value held at the time.

In the year 1856 A. Leonhardi, of Dresden, took out a patent for his so-called "alizarine ink." This was the first iron-gall ink produced in the form of a solution, and its invention completely revolutionised the ink-making industry.*

The discovery and manufacture on a large scale of coal-tar dyes (still also known as "aniline" dyes) led to further important advances, since the brightness of colour, the variety, and the properties of some kinds of these dyes, made it possible to prepare numerous new inks of every conceivable tint. The inventions of the hectograph, of inks for stamping pads, and of pigments for typewriter ribbons, were also made possible solely on account of the enormous colouring capacity of these dyes. Inks made from coal-tar dyes, however, have not altogether displaced improved iron-gall inks, for these have a number of extremely valuable and important properties, the most important of which is that they produce very permanent written characters; these are the inks dealt with first in this book.

* The priority for this invention is also claimed by an English firm.—C. A. M.

Many new and important recipes for the preparation of these different inks have also been incorporated in this new edition, so that the book not only gives a comprehensive survey over the whole field of ink manufacture, but also contains trustworthy formulæ for making inks of every kind.

III.

WRITING INKS.

In considering these inks it is necessary, first of all, to show what properties are required in ordinary writing fluid. A good preparation should have the following characteristics :—

1. *Depth of Colour.*—The writing must at once or very quickly show a strong and decided hue of the final colour that the ink is intended to produce.

2. *Freedom of Flow.*—The ink must flow readily from the pen, so that the finest lines and characters may be formed. It must not be thick, or form hard crusts when it dries upon the nib. This occurs sometimes with perfectly good ink, and is then merely a sign that the ink has become too concentrated by evaporation and requires dilution with water. If, however, the addition of water does not put the matter right, it proves either that the original composition of the ink was wrong, or that the ink has decomposed. This freedom of flow cannot, of course, be so perfect with copying ink as with ordinary writing ink. Copying inks are thicker and dry more slowly than ordinary writing inks. Complaints sometimes reach dealers from careless customers who have used copying ink when they had no intention of taking copies, and have found the two sides of a letter, for example, stick together so firmly that they were illegible when separated. Copying ink must always be diluted if it is to be used as a substitute for ordinary ink. It will not lose its special properties entirely even then.

3. *Durability.*—A good ink should keep its colour unchanged for a long time, and should not form deposits in the bottle, and in the form of writing on paper should not show any material alteration if the paper becomes damp or wet. This is a quality which comparatively few inks possess. A good ink must gradually dry in the air to a shiny brittle mass, and must not go mouldy, even after great dilution. This last condition is easily fulfilled. Many inks are of themselves toxic to moulds, and in any case antiseptics can always be added to them.

4. *Indelibility.*—For certain purposes, such as for documents that will possess a historical interest, it is necessary that the ink should be able to resist not merely the ravages of time, but also deliberate attempts to efface it by chemical means. To secure absolute indelibility is impossible, for resistance to every agent that could possibly be employed is a property that no substance we know of, or are at all likely to become acquainted with, possesses. While no ordinary writing ink, however, offers any considerable resistance to chemicals, certain inks, especially those which contain carbon as a pigment, are capable of withstanding them extremely well. Printers' ink, indeed, can only be destroyed by destroying the surface printed on as well. Printers' ink, however, can hardly be produced in such a condition as to be usable with a pen. Some dark-coloured substances of organic origin, the so-called humus-bodies, also resist the action of chemicals, although not so well as carbon.

The first three of these four qualities may be reasonably demanded of any ink professing to be a good one, and it is the business of the ink manufacturer to make inks possessing good colour, freedom of flow, and a reasonable degree of durability, and no others.

We can classify writing inks either according to colour or to chemical composition. The names red ink, blue-black ink, etc., are examples of the former method, and such terms as gallic acid ink, chrome ink, logwood (hæmatoxylin) ink, and others, illustrate the second. Several of these names, however, are misleading. Many inks are still sold as "alizarine" inks, for example, although madder or alizarine has long ceased to be used in the manufacture of that type of ink. As there is no advantage in adhering too strictly to any classification, the various inks are here described under their colours in an order depending partly on the method of manufacture and partly on similarity of the materials used. As black ink is the most important of all the writing inks, more space and attention is given to it than to the rest.

Black Writing Inks.

Black inks differ greatly in chemical composition, and can be divided into two sharply defined groups—those which contain tannin, and those which do not. The first class can be further divided, according to the raw material used, so that we have catechu-tannic acid inks, gall-nut (gallotannin) inks, etc. The inks free from tannin, or those that contain it with other substances, can also be divided on the same plan into chrome inks, alizarine inks, indigo inks, logwood inks, and so forth. The differentiation of the two main classes, however, is not absolute, as inks made from dyewoods, which we have put in the second class, often contain tannin. The black writing inks which have been longest known, and which are the most important, are the tannin inks, and they are the cheapest to manufacture. Originally these inks were very imperfect, for they were not solutions, but liquids, thickened by the addition of gum, sugar, etc., in which black compounds (iron tannates) were suspended in a elm and horse-chestnut, as well as sloes and buckthorn berries. This list makes no claim to be complete, but only give some of the better-known materials. It is possible to use any plant or part of a plant for making these inks, provided it contains a tannin that gives a black coloration with iron.

As a preliminary to a description of the properties of these tannin-containing bodies, some account of the chief chemical properties of the tannins themselves will be given, so as to enable the reader to understand the mode of formation of inks, and so to be able to make experiments for himself.

Tannins.

The tannins, sometimes incorrectly termed tannic acids, form well-defined groups of substances which are important constituents of many plants. They are divided into the two main classes—*pyrogallol tannins* and *catechol tannins*—according to whether they yield pyrogallol or catechol on decomposition. Usually the tannins occur in association or, possibly, in some cases, in combination with glucose, but recent investigation has shown that the tannin can exist in a free state apart from the glucose, and can be completely freed from it.

The properties of the tannins, considered as a class, are their astringent taste, their solubility in water, and their chemical capacity to form distinctive compounds with various substances. Thus they combine with gelatin to form an insoluble precipitate, and a combination of this kind takes place when hides are tanned. Advantage of this fact is taken for the determination of tannin by filtering the solution through prepared hide powder, which will retain the tannin in an insoluble form. Tannins also combine with the casein in milk, and with egg albumin; they also form compounds with many metals, but, from the point of view of the ink maker, the bluish-black or greenish-black compounds that they form with iron salts are the most important. Under certain conditions these iron tannates are soluble and form an ink; under other conditions insoluble iron tannates are formed and a precipitate will form. A change of this sort takes place when ink dries on paper, the soluble iron tannates being gradually acted upon by the oxygen of the air to form insoluble tannates.

GALLOTANNIN.

The best-known tannins are those formed in the remarkable excrescences known as galls produced on the leaves and twigs of various species of oak and other trees and shrubs, including the Chinese and Japanese galls formed on the leaves and stalks of different kinds of *Rhus*. These tannins are collectively known by the name of *gallotannin*, although they differ in their chemical constitution. When heated they all undergo decomposition, yielding a sublimate of pyrogallol.

The typical gallotannin, from Aleppo galls, is a pale yellow powder, which usually contains about 12 per cent. of moisture, a small percentage of gallic acid, and other tannin derivatives, and a small amount of glucose. It is readily soluble in water, alcohol, or ether, and belongs to the class of iron-blueing tannins, which are much more suitable than the iron-greening tannins for ink making.

The bark of the oak apparently contains tannins of both these groups, and is sometimes used as a raw material for the manufacture of a cheap ink, for which purpose, however, it is much less suitable than galls.

Gallic Acid.

This acid occurs ready-formed in divi-divi, in mango kernels, and, to a small extent, in galls, in which it is probably produced by decomposition of the gallotannin. If a decoction of one of these vegetable products in boiling water is allowed to cool, it deposits brown crystals, which, by solution in water, filtration through animal charcoal, and recrystallisation, become white. It is, however, much better to make gallic acid from galls by crushing them and leaving them in a damp state until the mould, which rapidly accumulates upon them, has converted the gallotannin, by means of a characteristic fermentation process, into gallic acid. This can then be dissolved out with water and purified by crystallisation.

Gallic acid is sharply differentiated from gallotannin by precipitating neither gelatin nor albumin. With ferrous salts it forms a deep blue solution, and on this property is based the value of gallic acid to the ink manufacturer.

Pyrogallol.

When gallic acid is kept at between 210 and 215° C. it is gradually converted into pyrogallol (pyrogallic acid). Distinctive properties of this compound are the precipitation of the metal from solutions of gold or silver and the formation of a bluish-black colour with proto-salts of iron.

It may be mentioned here that there is a sharp distinction between *ferrous* and *ferric salts*. Both contain iron and oxygen, but in different proportions, and they behave differently towards tannin. Ordinary ferrous sulphate (copperas) contains iron in the ferrous condition, but when treated for a short time with nitric and sulphuric acid it will contain only ferric iron.

Catechu-tannic Acid.

Mimosa catechu, a tree indigenous to India, provides an extract known to commerce as *cutch*. The special tannin of cutch (of which there are several kinds) is prepared by boiling it in water and adding sulphuric acid to the decoction. A precipitate is formed, which is a compound of catechin with sulphuric acid. This precipitate is mixed with carbonate of lead and boiled in water. The sulphuric acid remains undissolved as lead sulphate, and the catechin can be crystallised from the filtrate. A simpler method is to extract the cutch with ether. Catechin resembles gallotannin in some respects, but has a different chemical composition and differs also from it by giving a dirty green precipitate with solutions of iron salts.

Kinotannin.

This occurs in gum kino, and is a brown substance somewhat similar to catechin ; it forms a blackish-green compound with ferric salts. Fermentation converts it into kino red, the process being analogous to that which converts gallotannin into gallic acid.

Moritannic Acid.

This is deposited from a cooling decoction of fustic, the wood of *Morus tinctoria*. It has a sweetish astringent taste, and with ferrous salts gives a blackish-green precipitate. When heated it gives pyromoric acid as a decomposition product. Moric acid is a compound present in fustic, being probably formed by fermentation.

The tannins described above are particularly important on account of their action on solutions of salts of iron. Although this action is different with ferric and with ferrous salts, the difference is of little importance to the ink maker, for as all ferrous salts oxidise to ferric salts on exposure to the air, the final colour of the ink is always due to ferric iron. The following table shows the colours given by the various tannins :—

Tannin or Derivative.	Colour with Ferrous Salts.	Colour with Ferric Salts.
Gallotannin .	—	Blackish blue.
Gallic acid . .	—	Dark blue.
Pyrogallol . .	Blackish blue.	—
Catechin . .	Dirty green.	Dirty green.
Kinotannin .	—	Blackish green.
Moritannin .	—	Dark green.

To get a deep black ink we must always use a gallotannin or allied substance.

Since chemically pure tannins are too dear to be used, in practice one never gets any of the above-named colours in full purity, but always with a tendency to brown or black, owing to the action of the other substances present. This, however, is immaterial, as all that we require is that the colour should be very dark and also durable.

As the raw materials that yield the tannin for ink making are met with in commerce in very different conditions, it is necessary to give a more detailed description of them, to enable the purchaser to distinguish between good and bad consignments. Some account is also given of the preparation and properties of iron salts, which are also indispensable for the manufacture of tannin inks.

IV.

RAW MATERIALS OF TANNIN INKS.

Galls. Nut Galls.

Galls are morbid growths on the leaves of various kinds of oak caused by the sting of the gall wasp (*Cynips*), of which there are several species. The gall is formed round the egg of the wasp, which is laid within the young tissues of the plant, and the metamorphoses of the larva generally take place inside the gall, which is only deserted by the insect when it has reached its fully developed state ; then it bites for itself a hole of escape. In trade, the chief distinction made with galls is into pale and dark, but they are classified also as white, yellow, green, blue, and black galls. The best galls are those from which the insect has not escaped, i.e. which are unperforated, as those galls contain the highest percentage of tannin.

Good black galls contain up to about 77 per cent. of tannin, included in about 86 per cent. of soluble extractive. The form of the galls is nearly spherical, and their size varies from that of a pea to that of a small walnut. A good gall should be heavy and show a compact mass when cut through. If the gall is very light and filled with a crumbly mass it is of poor quality, as its content of tannin will be low. Experience has shown, too, that galls from southern countries are richer in tannin than those from the north.

The best galls are the Levantine galls, also called Aleppo galls. Next to them in quality are Morea, Smyrna, Marmora, and Istrian galls. In the third rank are the French, Hungarian, Italian, Senegal, and Barbary galls.

The signs looked for in the trade as denoting a good gall are almost perfect sphericity, a size not exceeding that of a cherry, a rough, unperforated exterior, and considerable weight.

Chinese galls which are produced on the leaf stalks, and shoots of a species of *Rhus* growing in China, India, and Japan, are formed by the action of a small aphis. They are of a very curious shape, whence they were once termed "Ears of India," and are hollow. The inside contains a débris of powder, in which the dead aphides can be distinguished under the microscope. Owing to their high content of tannin (about 70 per cent.) in relation to their total extractives (about 75 per cent.) Chinese galls are used for certain kinds of ink.

Japanese Galls resemble Chinese galls, and are also formed by an aphis, which may be identical with the Chinese variety. The galls usually contain less tannin (about 60 per cent.). The tannin differs in composition from that contained in Aleppo galls, have a smooth surface, often showing a reddish hue, and readily peeling off. Inside is a brown substance, full of the dead larvæ of insects.

Acorn Galls: Knoppern.

Aleppo galls are produced on the leaves and young stems of the oak, but there is a kind produced by a gall wasp that lays its eggs in the immature cups of the acorns. The result is the development of a gall instead of an acorn.

Knoppern are misshapen brown masses. They are harvested mostly in August, and the chief place of production is Hungary. The Bakony forest, between the Lakes of Neusiedler and Platten, yields an enormous quantity of knoppern. Large amounts come also from the oak forests of Asia Minor.

Knoppern come on the market both whole and crushed. Chemically they resemble the other galls, but contain a lower percentage of tannin (about 35 per cent.). They are extensively used in the leather, dye, and ink trades, being sold either in the whole or powdered condition.

Tanners' Barks.

The crushed bark of the elm, oak, pine, poplar, willow, etc., is largely used in tanning. The bark, after having been once used, is spread out by the tanners and dried for use again. The dried bark ferments, and its tannin becomes converted, more or less, into gallic acid. Hence the spent tan bark can be used as a raw material for the manufacture of cheap ink.

Tannin Extracts.

Tannin extracts, also sold as gall extract, myrobalan extract, etc., are either in the form of shining blackish-brown masses or of turbid liquids, having a very astringent taste. They are made by boiling in water galls, knoppern, myrobalans, fresh bark, and other vegetable substances rich in tannin, and carefully evaporating the decoction to a syrup, which, on cooling, sets to a brittle mass.

A good extract should consist in the main of tannin, and must dissolve completely in water without any carbonaceous residue, and give a very astringent solution. When not too dear they are excellent materials for ink making, and especially useful for manufacturers who have no space for storing large quantities of galls. Besides, the use of extracts simplifies the ink-making considerably.

It must be remembered that these extracts are very prone to turn mouldy in damp air. They should be kept in a dry room in casks or boxes lined with strong paper and with well-fitting lids.

In preparing the extract the tannin material is finely divided by means of crushing mills, and is then exhausted with water which is passed repeatedly over it in a vessel provided with a false bottom, or a battery of extractors is used in which each vessel can be connected with the others, and the extraction fluid, which can be heated if required, is made to circulate through them successively. Finally the extract is concentrated in vacuum pans.

Cutch and Gambier.

This is also known as Japanese earth (*Succus catechu* or *Terra japonica*). It is obtained in the East Indies by extracting the fruits and twigs of *Mimosa catechu* or dried plants with water and boiling down the decoction.

Yellow cutch (gambier) is sold in dice-shaped pieces, which yield their colour to boiling water and give it a sweetish astringent flavour. It is better for dyers and ink-makers than the brown product (cutch).

Brown cutch is closer and heavier than the yellow variety, and the dark brown, shiny, sticky lumps yield a reddish-brown decoction. Several kinds of brown cutch are known, and these differ considerably in their chemical composition

Cutch contains catechin and variable quantities of other soluble substances. The value of a sample from the point of view of the ink-maker depends mainly upon the proportion of the tannin (catechin) present. Recent analyses by Hooper of typical genuine samples of cutch have given the following amounts of catechin :—

Cawnpore catechu, 43·4; Surat catechu, 10·6; Shirval catechu, 13·8; Burma catechu, 12·4; and Burma catechu, 15·0 per cent.

Purified cutch is but rarely to be obtained. It is entirely soluble in water, and is to be preferred even to yellow cutch. The great demand for it led to the production of an adulterated extract in France. This so-called extract is called *cachou épuré*, and consists of brown catechu mixed with 40 per cent. or more of its weight of dried ox blood.

Gum Kino.

This is a brownish-red, brittle solid, which gives a beautiful reddish-brown solution with water or alcohol. The chief ingredient is "kinotannic acid." The following are the principal sorts found in commerce, with the name of the plant from which each is obtained :—

African kino	*Drepanocarpus senegalensis.*
East Indian kino . . .	*Nauclea Gamber.*
Columbia kino	Unknown.
Australian kino . . .	*Eucalyptus resinifera.*
Jamaica kino	*Cocoluba nucifera.*

The first of these is the best gum, but it is very rarely to be met with unadulterated. To denote its purity more precisely it is also called Gambia gum.

Fustic.

This is the wood of *Morus tinctoria*, and is indigenous to the West Indies. It contains moritannic acid. The sumachs, *Rhus coriaria* and *R. cotinus*, probably contain the same or very similar colouring matters as fustic. The fustics are used for yellow dyeing and also (with iron salts) for dyeing black. They give dark blackish-green inks.

We thus see that the whole manufacture of tannin inks turns on the colours which the various tannins give with iron. Hitherto the expense of purification has prevented the extensive use of pure tannins in ink making, and has hence made it difficult for manufacturers to determine exactly the proper proportions of iron salt and tannin to give the best results in practice.

Myrobalans.

Myrobalans is the trade name given to the dried fruit of various species of Indian *Terminalia*, the chief source being the *Terminalia chebula*.

The ovoid fruit when perfectly dry is reduced to nearly half its original size.

During the drying process it becomes ridged, and then the outer layer of the pericap is hard enough to resist the blade of a penknife.

A small percentage, however, does not become ridged, and in such cases it is found that almost the whole of the interior of the fruit has turned into a black powder, which is much valued for making ink.

The best uniform qualities are the No. 1 Bhimley and No. 1 Rajah, both of which are very rich in tannin—35 to 38 per cent.

The low price of myrobalans and the abundance obtainable have induced the makers of ink to use them freely, especially after roasting. Owing to the large amount of extractives other than tannin which they contain they are particularly suitable for the manufacture of copying inks.

Nitrous acid reacts on the red colouring of the fruit, changing it to blue.

TANNIN: TANNIC ACID.

In addition to the above-mentioned raw tannin materials more or less pure preparations of tannin (tannic acid) made from them are now used to a considerable extent in the manufacture of ink. They are prepared by extracting a powdered tannin material, such as Aleppo or Chinese galls, with a mixture of ether, water, and alcohol. This extracts not only the tannin, but also other constituents of the substance (gallic acid, glucose, colouring matters, resins, etc.). To obtain a purer product the syrupy extract is shaken with twice its volume of ether, and the ethereal extract, when evaporated on the water bath, leaves a cream-coloured to brown residue, which is readily soluble in water.

Although such tannin is dearer than the same amount of tannin in the raw materials, it offers many advantages to the ink manufacturer, enabling a uniform product, and one that throws down very little deposit in the maturing vats, to be obtained.

It will thus be seen that the manufacture of tannin inks turns on the colours which the various tannins give with iron salts, some producing dark blue, others dark green colorations or blackish tints. The second main constituents of these inks are iron salts.

COPPERAS: GREEN VITRIOL.

This is offered for sale in the form of large and beautiful sea-green crystals, which have an unpleasant, metallic, astringent taste, dissolve easily in water, and, by long exposure, crumble to a rust-coloured powder of basic sulphate. Green vitriol is now so cheap, being a bye-product of several chemical manufactures, that it does not pay the ink-maker to prepare it for himself. For experimental purposes, however, the salt may be prepared free from ferric iron as follows: Pour dilute sulphuric acid on old nails, hoop-iron, or other scrap, and as soon as the evolution of hydrogen gas has ceased, filter the solution while it is still warm (it becomes hot of its own accord), and mix the filtrate with its own volume of strong spirit. The spirit throws down a pale green powder, which is practically pure ferrous sulphate. The precipitate is filtered off, dried in filter paper, and kept in a closely stoppered bottle.

Inks made with ferrous sulphate in time contain ferric as well as ferrous tannate, formed by absorption of oxygen from the air. Those made according to antiquated recipes, by mixing solutions of iron in strong vinegar with decoctions of galls, are also ferrous inks, and probably contain both ferrous tannate and ferrous acetate. Commercial copperas is usually bought on the basis of its content of iron. The pure salt contains approximately 20 per cent., but "rusty" basic salts may contain 24 per cent. or more. The amount in a good average sample is about 19 per cent.

Ferric Sulphate.

This is prepared by mixing a solution of green vitriol with a little nitric acid, and boiling. Unless too much nitric acid has been used, we get a rusty-looking precipitate, because ferric oxide requires more sulphuric acid to dissolve it than ferrous oxide. This precipitate is basic ferric sulphate. We can either filter off, or carefully add sulphuric acid and warm it until it redissolves. The addition of any excess of nitric acid is to be avoided, as free nitric acid will gradually bleach ink made with solutions containing it.

These pure salts are only worth preparing for use in original experiments, as they cost too much to be used in preparing ink for sale. Such experiments should, however, be made by every ink manufacturer who wishes to improve his business, especially if he wishes to work with tannin material with which he is not familiar. Ferric sulphate should be free from excess of sulphuric as well as of nitric acid, as acid fluids behave to tannins very differently from liquids not containing an excess of acid.

V.

THE CHEMICAL CONSTITUTION OF THE TANNIN INKS.

THE tannins are generally used in the form of the raw material. Hence the iron combines not only with the tannin, but also with other substances present in the vegetable product, whereby the colour and other properties of the ink are modified.

According to the extensive researches of Bostock, which, however, were carried out a considerable time ago, the following reactions take place when a decoction of galls is mixed with a freshly prepared solution of ferrous sulphate.

The ferrous iron combines with the gallotannin, gallic acid, and mucilage, and with the extractives. The compounds with the acids are those which give the necessary colour, but the others deserve attention for several reasons. It is these which often make an ink flow too thickly, and which impart the tendency to mould. Moreover, an ink which contains combinations of iron with mucilage or extractives also quickly loses its colour, and deposits a black sediment consisting of those compounds. Its precipitation leaves the ink almost colourless, as it entangles and carries down with it the coloured particles of tannate of iron, which, while suspended in the liquid, give the colour to the ink.

Many experiments show that the gallotannin and gallic acid are the only constituents of gall decoction which are of any value to the ink maker. If, for example, a cold infusion of galls is made and then kept boiling for a long time, a flocculent precipitate is formed, which consists of extractives coagulated by the boiling. If it is filtered off and the clear solution is exposed to the air, it becomes very mouldy in a few days. The mould-fungi develop on the solution, and thereby produce in it important chemical changes. They convert the gallotannin into gallic acid, and destroy the soluble extractives almost entirely. In a few weeks, indeed, the liquid may be regarded as a fairly pure solution of gallic acid. If it is then filtered and boiled to kill the mould spores, a liquid is obtained which gives with solution, of ferrous sulphate a fine blue-black ink, which will keep for months in an open vessel without showing the least sign of mould. The ink will, however, gradually turn pale and deposit a black sediment, because the fluid is not dense enough to keep in suspension the tannate of iron that is formed. These experiments show that the tannate and gallate of iron are present in an oxidised ink, not in solution, but in the solid state. The liquid must therefore be dense enough to keep the particles from settling, and, if necessary, bodies must be added which, while without action on the colour, augment the density. For this purpose either gum-arabic or dextrin is used, and also, although it is a less suitable substance, sugar. Dextrin is much cheaper than gum-arabic, but has the great fault of being hygroscopic, so that the ink dries slowly on the paper. The use of sugar is inadvisable, not only on account of its price, but also because it favours the growth of mould, which may convert the ink into a thick stringy mass which can no longer be used.

In writing with inks made with ferrous sulphate it will be observed that the letters are at first bluish or greenish, but turn to a deep black in time. This change of colour results from the oxidation of the ferrous to ferric tannates, which have a darker colour than the ferrous compound. If the ink is made with ferric sulphate it writes black at once.

On account of the variable amounts of tannin contained in the raw materials, it is impossible to calculate the amount of iron salt required for any given weight of galls, oak bark, etc., without a chemical analysis to determine the tannin. Hence recipes show great differences in the relative quantities given. In the author's opinion nearly all recipes prescribe the use of much too large quantities of ferrous sulphate, and thus when the writing turns yellow or rusty the cause is often to be found in the presence of an excess of iron salt which gradually decomposes the black tannate, so that at last nothing is left on the paper but basic ferric sulphate. This substance is also the cause of the yellow marks seen on linen which has been stained with ink and then repeatedly washed.

According to experiments which have been made on the properties of various inks in connection with the relative amount of galls and ferrous sulphate used in their preparation, it has been found that equal weights of galls and ferrous sulphate gave a very fine black ink, but that the characters soon turned brown and rusty. With still larger quantities of copperas, the ink is still black, but very deficient in keeping power. The reason of this is that such an ink contains copperas in an unchanged state. This oxidises on the paper, forming the brown basic sulphate. This brown coloration can be easily obtained by simply writing with a solution of ferrous sulphate alone. The freshly dry letters are invisible, but exposure to the air soon converts them into the brown basic sulphate.

It will be found, on the other hand, that quantities of ferrous sulphate much less than the weight of the galls will still give a good deep black ink, for the extremely finely divided state of the tannate of iron gives it such great colouring power that a small quantity only of it is needed.

If we write on paper with decoction of galls only, the writing is at first hardly visible, but in time it will become brown, and easily legible. In one special case, however, mentioned on a later page, the writing may disappear altogether. The tannins have the property of being gradually converted on exposure to the air into brown compounds, possibly akin to the humus-bodies which are present in the soil and in rotten wood. This change is greatly hastened by the presence of alkalies. Since paper always contains more or less lime, this alkali helps the formation of these substances and the appearance of the writing. If the writing done with gall decoction is wiped over when dry with a sponge just damp with solution of washing soda, the brown letters will appear very quickly. But when the paper contains free chlorine, the writing will develop feebly or not at all. Such paper will destroy the colour of even the very best ink in time, as no organic dye can withstand chlorine. Such badly made paper also contains the seeds of its own destruction.

It is thus not difficult to decide whether an ink should contain an excess of iron salt or an excess of tannin. In the first case it will turn brown, and become nearly illegible. In the second it will remain black for a very much longer period. It must not be forgotten, however, that an excess of organic matter makes the ink liable to mould, even after it has dried on the paper, so that the colour fades. Hence a preservative must be added to such inks.

The antiseptic agent most used by ink-makers is phenol (carbolic acid), which is very cheap and is an unsurpassable preservative for all inks.

Pure carbolic acid crystallises in long colourless needles, having a very penetrating odour, and is easily soluble in water. The presence of as little as one-hundredth per cent. of carbolic acid will act as a perfect preservative. As the acid evaporates slowly when exposed to the air, however, rather more than this proportion should be present in an ink, but never so much that its smell becomes perceptible. The phenol may be made to contribute somewhat to the colour of the ink, as it forms a violet compound with ferric sulphate.

Another preservative used by ink manufacturers is salicylic acid, which is as effective as carbolic acid, and which also gives a violet coloration with iron salts.

It is probable that the excessive amounts of sulphate of iron which we find in nearly all the older recipes are intended to act partly for preserving purposes, as the salt is a disinfectant itself. We have, however, pointed out the very grave objections to using excess of iron salt in a tannin ink. No one nowadays, when we have such a perfect preservative as carbolic acid, would think of making the iron salt do the work of an antiseptic as well as that of a colouring agent.

The tannin inks are the most liable of any to decompose, but carbolic acid should be added both to them and to inks of every kind as a preservative. The expense is very trifling, and the value of the addition can be appreciated by any one who will reflect that it absolutely guarantees that none of the ink which he manufactures will become mouldy or decompose, either in his hands or in those of his customers. An exception to this rule is found in the case of the aniline inks, which require no preservative, the dye itself being one.

As regards the amount of carbolic acid to be employed, 1 lb. will preserve 1000 gallons of ink. For the sake of perfect safety, however, more is used, say from 4 to 8 lb. per 1000 gallons.

VI.

RECIPES FOR TANNIN AND FERROUS SULPHATE INKS.

(*N.B.—The quantities given in recipes in this book are in parts* BY WEIGHT *unless the contrary is distinctly stated.*)

FEW recipes comprise simply the tannin material, iron salt, and thickening agent. Most of them mention other ingredients, although it is often impossible to see what influence these can have on the colour of the product.

In the following pages is given a collection of excellent recipes, beginning with copperas and tannin inks, which have long been made of first-rate quality, and then proceeding to other tannin inks.

A.—PURE TANNIN-IRON INKS.

Brande's Gall Ink.

Aleppo galls	3
Crystallised green vitriol (copperas)	2
Gum arabic	2
Water	60

This ink is made cold. The crushed galls are placed in half the water, while the gum and the copperas are dissolved separately in the other half. This solution is then poured into the vessel containing the galls. The resultant liquid can be used as ink at once, but it does not fully oxidise and acquire its deepest colour before the lapse of about two months. During this time it is occasionally stirred, and then, when the coarser particles have settled, the ink is bottled. The residue of the galls can be used again, and will make a good ink with—

Copperas	$\frac{1}{2}$
Gum	$\frac{1}{2}$
Water	15

This method of manufacture is extremely simple, but one or two modifications greatly improve it. As the presence of the woody fibre of the galls is injurious, they should be placed in a bag which should then be hung in the water with two-thirds of its bulk immersed. Under these conditions the tannin is very rapidly extracted, and all insoluble matter remains in the bag.

There are also many other extractives from the galls in the ink, which is therefore very liable to mould and to thicken. When this phenomenon occurs the whole ink is converted into an oily mass that can be drawn out in threads and clings to the nib, so that writing becomes impossible. Frequently this fault cannot be remedied by filtration, but in most cases it can be cured by boiling it up with one-twentieth of its volume of strong gall decoction for two or three minutes.

As the result of numerous experiments and tests the author has so far improved Brande's ink that it responds fairly well to all that can be demanded of a cheap product. The ink must be regarded as a cheap ink only, but it is an excellent writing fluid if a very dark colour is not essential.

Improved Brande's Ink (*Lehner*).

Galls or knoppern	1,200
Ferrous sulphate	800
Gum arabic	800
Water	24,000
Creosote	3

Cover the galls with part of the water, and dissolve the gum, copperas, and creosote separately in the rest of the water. Pour the solution on to the galls, and cover up the vessel. Stir every day for about three weeks, when the ink will have reached its full blackness, and can be bottled off. This ink will keep for years.

Ure's Tannin Ink.

This is a very deep black and very durable :—

Galls	18
Ferrous sulphate	8
Gum	7
Water	145

The galls are crushed to a coarse powder and vigorously boiled for two hours with 130 parts of the water in a pan, the mixture being continually stirred to prevent burning, while more water is added from time to time to replace that lost by evaporation. The decoction is then allowed to cool, and filtered through a linen cloth, of double or treble thickness if necessary, and sometimes with a filter paper inside. The cloth is suspended by the frame shown in Fig. 1, the spikes going through the linen, so as to form a bag. While the filtration is proceeding the copperas and gum are dissolved in the remaining 15 parts of water, and the solution poured into the filtrate.

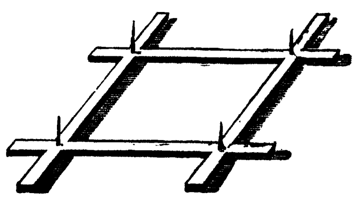

FIG. 1.

The ink does not develop its full blackness at once, and it is therefore best to keep it in a partly filled vessel, so that the air can act upon it. To make it keep, a little carbolic acid should be added, or some oil of cloves, or even a little gas-tar. Carbolic acid, however, is the best thing to use.

English Counter Ink.

Galls	20
Ferrous sulphate	5
Gum	5
Water	240

The water is divided into three parts—100, 80, and 60 respectively. The galls are boiled in the largest portion for $1\frac{1}{2}$ hours. The decoction is poured off, and the second lot of water is boiled on the galls for an hour. It is then replaced by the smallest lot of water, which is boiled on them for half an hour. The first two decoctions are mixed, and the third is used to dissolve the copperas and the gum. The whole is then mixed.

This practice of boiling the galls with several lots of water is highly to be recommended, as it ensures complete extraction. The ink is finally mixed with a little carbolic acid, and stirred once a day for a week. The ink becomes clear in a few more weeks and is then bottled.

To tell when an ink has cleared, i.e. that nothing remains suspended but the necessary colouring matter, mix some of it in a tumbler with water till it is transparent. No solid particles must then be visible to the naked eye, and on long standing a soft black sediment should form at the bottom, while the supernatant liquid is only pale yellowish-brown.

American Counter Ink.

Gall	24
Ferrous sulphate	5
Gum	5
Water	200

The peculiarity of this ink consists in the fact that some of the copperas is oxidised by roasting the whole of it before use. This is done over a fire in an iron, or better in an earthen, pan. The copperas first loses its water of crystallisation and becomes white. It afterwards turns yellow from the formation of ferric sulphate. Over-heating converts some of this into the basic sulphate, which, being insoluble, is waste. The roasting process has therefore been somewhat modified with the best results. Two parts of water are mixed with one of concentrated sulphuric acid, and the mixture poured over twenty parts of ferrous sulphate. The whole is then slowly heated to the fusing-point of lead (334° C.). We thus obtain a substance perfectly soluble in water. Care must be taken that the heat expels all excess of sulphuric acid from the mass or the ink will strongly corrode steel nibs, and be useless.

Karmarsch's Gall Ink.

Galls	18
Ferrous sulphate	7
Gum	7
Water	64

The solids are powdered and left for a week in three-quarters of the water, with one daily stirring. The rest of the water is then added, and the ink is fit for use.

This ink is very good and cheap, but readily becomes mouldy, and should therefore be mixed with carbolic acid or with oil of cloves, which is an antiseptic and has a pleasant smell.

Gall inks attack nibs when not quite free from acid. Hence some recipes contain an alkali. An example of these is—

Link's Steel Pen Ink.

Galls	224
Ferrous sulphate	96
Gum	80
Water	3200
Ammonia	2
Spirit	128

The ammonia is to neutralise the free acid, and the object of the spirit is to prevent mould and to mask the smell of the ammonia. In the author's opinion the spirit is quite superfluous, as it not only adds to the prime cost of the ink, but also makes the ink dry up. The following formula gives a better product :—

✓ *Link's Steel-Pen Ink (Improved by Lehner).*

Galls	112
Ferrous sulphate	48
Copper sulphate	2
Gum	40
Water	1600

When the ink is made it is treated with ammonium carbonate so long as a strong effervescence is caused. The reason for adding the copper sulphate is that this salt covers a new nib dipped into the ink with a coating of copper, which protects it, as copper is much less easily corroded than steel. At all events, the surface of the nib is thereby prevented from rusting, but the point very soon loses its copper coating through friction against the paper.

B.—Gallic Acid Inks.

The gallic acid inks combine with a beautiful blue-black colour the valuable property of being far less liable to decomposition than those made from gallotannin. The special feature of the manufacture consists in the preliminary conversion of all the gallotannin into gallic acid. This is done by simply allowing the galls or their decoction to ferment spontaneously. It is, however, often very inconvenient to have a big vat of decoction standing fermenting for weeks together. Hence the following very practical method of simplifying the process may be used. A vat is nearly filled with the coarsely powdered galls or bark, and just enough water at from 20° to 25° C. is then poured on to cover the mass. The contents of the vat mould very rapidly, becoming covered with a grey-green pellicle, which extends into the interior of the inside of the mass as white filaments. The conversion into gallic acid is complete in from eight to ten days, when, to prevent further action, boiling water is poured over the mass to kill the ferment, or enzyme, as it is now termed. The solution of gallic acid is then drawn off by means of a cock. It gives ink of a fine blue-black colour and of great durability.

The names under which these gallic acid inks come on the market are as various as the recipes for making them. The following are some of the best :—

First Quality Gallic Acid Ink.

Gall nuts	50
Ferrous sulphate	10
Gum	10
Water	2000
Carbolic acid	2

The crushed galls are soaked in the water and allowed to ferment. This often takes some time, especially in the winter. It is a good plan to inoculate the mass with the mould from a piece of mouldy bread or leather. The fermented liquid is filtered, and the other ingredients dissolved in it.

Runge's Gallic Acid Ink.

Galls	8
Water	64
Ferrous sulphate	4
Gum	2

The larger part of the water is poured boiling over the crushed galls, which are then allowed to ferment for two months. The liquid is then drawn off, and the residue is rinsed with the rest of the water. The two solutions are filtered together, and the gum is dissolved in the filtrate. The copperas is then added in the form of concentrated solution.

Bolley's Inks.

Bolley, who was professor in the Technical High School at Zurich, published the following recipes, which show how widely even chemists may differ in their views as to the right proportions for the ingredients of ink :—

1.

Galls	125
Ferrous sulphate	24
Gum	24
Water	1000

This, according to the author's experience, gives a good ink, but contains galls in excess.

2.

Galls	66
Ferrous sulphate	22
Gum	19
Water	1000

Here the proportion of copperas to galls is correct.

3.

Galls	62
Ferrous sulphate	31
Gum	31
Water	1000

In this there is an excess of iron salt, and ink made from the recipe turns yellow sooner than those made from the first two.

STARK'S INK.

Boil 100 oz. of Aleppo galls with 8 gallons of water, and dissolve in the decoction from 33 to 50 oz. of gum. When cold, add 66 oz. of ferrous sulphate, 66 oz. of indigo-carmine, and 1 oz. of carbolic acid. This is a beautiful ink, but the indigo-carmine makes it an expensive one.

CHEAP GALLIC ACID INKS.

1.

Galls	100
Logwood	30
Dextrin	40
Alum	12
Ferrous sulphate	45
Soft water	1000

2.

Galls	58
Dextrin	40
Ferrous sulphate	45
Soft water	300

3.

Japanese galls	180
Dextrin	120
Ferrous sulphate	85
Indigo-carmine	90
Water	2500

4 (*School Ink*).

Japanese galls	30
Water	720
Dextrin	36
Ferrous sulphate	10
Pyroligneous acid	2
Logwood extract	28

Extra Cheap Iron Inks.

Leather cuttings can be used with great advantage for the manufacture of glue and ink. The cuttings are covered with water containing ½ per cent. of hydrochloric acid, and left for a week. The liquid is then run off, and as much as possible is squeezed out of the leather. The leather is then treated for another week with another lot of dilute acid. The solutions are filtered and mixed, and enough ferrous sulphate is added to make letters written with the ink turn a deep black in a few hours. The ink is then exposed to the air for several weeks, to darken it, and finally bottled. The leather residues are first soaked and then boiled in water, and will yield a very good if rather dark-coloured joiners' glue, for which it may be possible to find a market.

VII.

FERRIC INKS.

As already stated, many inks only acquire a deep black colour a considerable time after the writing has been done. The change is due to the oxidation of the ferrous to ferric tannate. As a necessary consequence of this many attempts have been made to use ferric salts only in the manufacture, so as to get an ink which will write a deep black from the first. The chief method is to roast the ferrous sulphate, i.e. to oxidise it by heating it in the air, before it is used. The author's experiments, however, have shown that inks containing ferric iron only are of very little value. The ferric sulphate was prepared by boiling a solution of the ferrous salt with nitric acid or by dissolving the sesqui-oxide in sulphuric acid.

On adding to the ferric salt a decoction of galls, fermented or unfermented, and with or without logwood, an ink was obtained which wrote at once with a perfect lustrous black, but in time the characters lost their lustre and became of a brownish hue. Worse than all, however, the ink adhered so loosely to the paper that with a little care the writing could be entirely erased with a damp sponge. It was only after some years that the ink withstood the sponge to some extent. It is conceivable that the ferrous compounds penetrate the paper more deeply than the ferric salts, so that when the persalts are formed on the paper they are formed below the surface, and are hence protected by the fibre from removal with water. The browning of the writing done with a ferric ink is probably due to separation of part of the sesquioxide; this in the free state shows the reddish-brown colour which is so familiar in rust.

Japan Ink.

This ink, which was formerly in great demand, consists in the main of ferric tannate. It is made by roasting green vitriol at a moderate heat and then treating it with logwood extract and decoction of galls. It is of a deep black at first, but has all the drawbacks above noted as belonging to ferric inks. Like all other ferric inks, too, it does not flow very freely, and the nib must be carefully cleaned after use or it will soon be so encrusted as to be unusable.

The best iron inks are those containing both ferric and ferrous compounds. It is not necessary, however, to have the ferric compound ready-formed in the ink; writing done with an ink made solely from ferrous sulphate soon comes to have the necessary amount of ferric oxide in it to make the writing black by spontaneous oxidation on exposure to the air.

Ink for Fountain Pens.

Tannin	90
Gallic acid	30
Ferrous sulphate	60
Ferric chloride solution	30
Indigotin	45
Gum arabic	3·6
Carbolic acid	3·6
Water	4500

The tannin and gallic acid are dissolved in about 3500 parts of warm water, and the other constituents in the rest of the water. The two solutions are mixed, and the ink filtered after standing for two weeks.

VIII.

BLUE-BLACK INKS: ALIZARINE INKS.

If the name shows anything, these inks should contain alizarine. Alizarine is a red colouring matter occurring in madder (*Rubia tinctoria*), but it is now always prepared artificially. It is very largely used in dyeing, especially in Turkey-red dyeing. Nevertheless, most of the so-called "alizarine" inks contain neither alizarine nor any other constituent of madder.*

The inks so far described owe their colour to the presence of suspended and very finely divided tannates or gallates of iron. The sole object of adding gum is to keep the coloured precipitate in suspension, and if it is omitted a black precipitate will soon form in the ink. The formation of this sediment can, however, be completely prevented by adding an acid to the ink. For this purpose acetic acid is specially suitable, and we have here the secret of what are called "alizarine" inks. They are simply iron inks in which any precipitation of tannate of iron is prevented by acidification with acetic acid, or more commonly, with sulphuric or hydrochloric acid. The solution has generally

* The name originated with some of the inks patented by Leonhardi in 1856. These contained both indigo and madder, but the latter was soon dropped as superfluous. By that time, however, the name "alizarine" had become fixed in the public mind as descriptive of the type of ink. It is no longer used in this country, and this sort of ink is best known as "blue-black" ink.—C. A. M.

a rather pale greenish or brownish colour, and the writing is at first green, turning in a few hours to a fine black. The process of blackening takes place in two stages; the acetic acid evaporates in part, leaving the solid matter it had in solution behind it. Another part of the acid is neutralised, partly by the lime in the paper, but chiefly by the traces of ammonia in the atmosphere. There is always lime in paper, from the water used in its manufacture. If a wet writing with an alizarine ink is put under a bell-glass with a dish of ammonia, the writing becomes black almost instantly.

Of course, an ink which contains so strong a free acid as acetic or sulphuric must corrode steel nibs rapidly, but that need only happen to such an extent the first time the nib is used. If the ink is then allowed to dry on the nib it forms a protective coating which checks further action. Naturally, all excess of free acid should be avoided in the manufacture, if only for the sake of economy. An ink which has been accidentally made too acid may be brought to the right point by the cautious addition of ammonia. If too much alkali is added the object of adding the acid is lost, for it all becomes neutralised and solid matter appears in the ink. In that case more of the excessively acid ink can be added. The best plan of all is to divide the ink which is too acid into two parts. One is then made neutral with the ammonia, and mixed with the other.

The "alizarine" inks have gained their popularity partly because they leave no sediment, even when they have stood for years in bottle, and partly because they flow very freely from the pen—a matter of great importance for quick writing. The great objection to them is their pale colour. In some cases the fresh writing is barely visible. This fault can be remedied by adding just enough of a solution of a very powerful dye, which is, in its turn, masked when the ink turns black. Before the discovery of the water-soluble aniline dyes, indigo-carmine was the only substance available for this purpose. Until the artificial dyes were invented indigo-carmine and cochineal carmine had the greatest colouring power known, and both were therefore much used by the ink-maker in spite of their high price. In fact, no other dye is so suitable for inks as indigo-carmine, but we have now artificial dyes, smaller quantities of which will serve the same purpose, and they have therefore replaced it to a large extent. It is, however, still extensively used in writing inks, and, in addition, forms in itself an excellent ink both for writing and for stamping.

Indigo-Carmine.

Indigo is the splendid blue dye obtained by a fermentative process from plants of the *Indigofera* species indigenous to India and other tropical countries. Very many kinds of indigo come upon the market, those sold under the names of Spanish and Bengal indigo being considered the best.

Indigo has a deep dark-blue colour and a characteristic coppery lustre. The following tests of good quality should be carefully noted: The pieces must be light, and of a uniform colour, and show a uniform fracture. Sand and pebbles must be absent, and on rubbing with the finger-nail the coppery lustre must appear distinctly. The pieces must not feel damp. They are often sprinkled with water to add to the weight.

To prepare indigo-carmine the indigo is dissolved in sulphuric acid. This can only be done in the fuming or Nordhausen acid, and only when the indigo is quite dry. The indigo is finely powdered (it is a mistake to buy indigo ready ground, as it is then usually adulterated), and dried with the greatest care at a temperature which must not exceed 120° C. The acid is then poured on to the indigo while it is still warm. The quantity needed depends upon the purity of the indigo and on the strength of the acid. It is usually about four times the weight of the dry indigo.

The acid must be added slowly, with constant stirring with a glass rod, and the indigo must be in a roomy earthenware basin, because the act of solution is accompanied by much frothing. When all the acid has been added the basin is left covered for twenty-four hours. By that time the conversion of the indigotin into sulpho-indigotic acid is complete, and the new compound can be converted at once into indigo-carmine, which, however, is not pure, being contaminated with substances that have been carbonised by the sulphuric acid. To get pure indigo-carmine we dilute the liquid with ten or twelve times its volume of pure water and allow it to stand for a few days, till all the insoluble matter has settled to the bottom. The clear solution then looks black in large volumes, but in thin layers it is transparent and of a splendid blue colour. It is decanted and evaporated without boiling, and at the same time neutralised with potassium carbonate. As soon as the effervescence, due to the escape of carbonic acid, has ceased the liquid consists of a solution of pure indigo-carmine, which is potassic sulpho-indigotate. This salt can be separated in the solid state by very cautiously continuing the evaporation, but it is more usual to precipitate it with sodium carbonate, on the addition of which the indigo-carmine, being less soluble in alkaline solutions than in water, is thrown down. It is filtered off and dried, and then shows an efflorescence due to the excess of sodium salt.

Indigo-carmine, when dry, has a deep blue colour with a strong coppery lustre. It is extremely soluble, and a very small quantity of it gives an intense blue colour to the water. It is with difficulty soluble in alcohol or in saline solutions.

For ink making it is quite unnecessary to evaporate the solution of indigo-carmine. As soon as the neutralisation with potassium carbonate is finished, the solution should be concentrated and preserved in bottles. It is, however, required in a solid state for water-colour painting and as a laundry blue, or for india-rubber stamps. The above-mentioned efflorescence spoils the look of the solid substance, and can be prevented by adding glycerin to the mass. The hygroscopic qualities of the glycerin prevent the salt from efflorescing, so that the indigo-carmine permanently retains its dark blue shade. The process patented by Leonhardi in 1856 was as follows: Aleppo galls (42 parts) and Dutch madder (3 parts) were extracted with sufficient water to yield 120 parts of liquid. This was filtered, and to the filtrate were added $1\frac{1}{8}$ parts of indigo solution, $5\frac{1}{8}$ parts of ferrous sulphate, and 2 parts of a pyroligneous acid solution of iron. As with all these inks, indigo or another dye (aniline dyes) forms the "provisional colouring matter," whilst the true pigment, the iron tannate, is not formed until later.

Counter "Alizarine" Ink.

Galls	20
Ferrous sulphate	12
Gum	2
Acetic acid	200
Indigo-carmine solution	40

This green, readily flowing ink is made by soaking the powdered galls in the acetic acid, drawing off the solution after a few days, and dissolving the copperas and the gum in a part of it, which is then added to the rest. Finally the indigo-carmine is added. It is best not to weigh it, but to add it gradually in the form of a solution till the ink writes a fine bluish-green at once. The ink is bottled as soon as this point is reached, and forms a clear dark-green solution.

Many ink-makers use sour beer vinegar instead of acetic acid, and thus get an ink which soon moulds on exposure. To avoid this, and at the same time save expense, crude pyroligneous acid should always be employed. The carbolic acid in this prevents any mould from growing.

First Quality "Alizarine" Ink.

Galls	40
Iron solution	15
Indigo-carmine	5
Gum	10
Pyroligneous acid	10
Water	100

This is the best of all "alizarine" inks, because it has little action on steel pens; it is prepared as follows:—

The galls are powdered and soaked in the water and half the acid for eight days. The gallotannin is thus completely extracted, but none of it converted into gallic acid, as the pyroligneous acid prevents any fermentation. The iron solution is prepared from pyroligneous acid and scrap iron, left together for eight days. This solution must contain enough acid to keep the acetate of iron in solution. To test this point a sample of the gall infusion is mixed with one-tenth of its volume of the iron solution. The thin column of the mixture should be clear and of a dark-green colour, but if the column is black and opaque more acetic acid is necessary, and the additional amount required must be ascertained exactly by adding measured quantities of pyroligneous acid, with constant stirring, till the liquid assumes the appearance described. From this the extra amount wanted for the whole lot of ink can be calculated. Any necessary extra acid is then added to the gall infusion, the gum is dissolved in it, and the iron solution is then put in. Finally, enough indigo-carmine is added to give the required shade.

"Alizarine" Indigo Ink.

The following is Prollius and Bley's recipe:—

Galls	10
Indigo	1
Fuming sulphuric acid	4
Iron filings	2
Chalk	2
Water	80

Boil the crushed galls with the water until 40 parts of infusion have been obtained. Dissolve the indigo in the acid, add 40 parts of water to the solution, and then put it into the gall infusion. Next introduce the iron filings, which will dissolve with evolution of hydrogen, and the ferrous sulphate formed will react with the gallotannin. The excess of sulphuric acid is then precipitated as calcium sulphate by means of the chalk. A still better plan is to dissolve the iron in the indigo solution first, neutralising them with chalk, and adding the gall infusion after decantation from the calcium sulphate. The reason is that in the method first mentioned the calcium sulphate carries down with it some of the colouring matter of the ink. This method is simpler, but more expensive than using sulphate of iron ready made.

American "Alizarine" Ink.

Powdered galls	40
Ferrous acetate	15
Gum	10
Pyroligneous acid	10
Indigo-carmine	5
Water	100

We could give many more recipes for these inks, but they simply vary from those given and about to be given in the proportions of the ingredients, without yielding any better inks.

Real Patent "Alizarine" Ink.

Aleppo galls	42
Dutch madder	3
Indigo-carmine	1
Ferrous sulphate	5
Acetate of iron	2

The galls and madder are boiled with water down to 120 parts of solution, and the other ingredients are added after filtering. The addition of the madder makes very little difference to the beauty or the durability of the ink, and it is now very difficult to get madder, which has been almost completely replaced by artificial alizarine.

Hager's "Alizarine" Ink.

In a roomy earthen dish (to allow for frothing) put 12 parts of fuming sulphuric acid, and add to it, little by little, 2 parts of indigo. Twenty-four hours after the indigo is all in, dilute with 16 parts of water, and dissolve in the solution 6 parts of clean iron filings. In the meantime boil 24 parts of Chinese galls with 300 to 400 parts of water, and dissolve 6 parts of gum and 3 of sugar in the decoction.

Then add the other solution and a little carbolic acid for preservative purposes.

As good results can be obtained with very various proportions of tannin materials and iron salts, it is superfluous to multiply recipes for iron inks. Every intelligent maker can soon discover wherein any recipe which he uses is faulty, and a few experiments will then quickly show him what are the best proportions, both as regards the cost and the quality of his ink, of the particular materials at his disposal.

IX.

EXTRACT INKS.

THE fact that gall-nuts are usually prescribed in ink recipes as the ingredient for providing the tannin is owing to an old but erroneous idea that they contained a sort of tannin absent from all other vegetable matter. It must be regarded as a great step in advance that we have learned to use other vegetable substances to prepare inks which are in no way inferior to those made from galls. An ink maker who knows his trade can get his tannin very cheaply indeed, by using some of the materials to be presently named. In the first rank of these are the unripe fruits of the sloe (*Prunus spinosa*), of the bird-cherry (*Prunus padus*), and of the black elder—any fruits, indeed, which have an astringent taste or intense colour.

Most of the barks of our forest trees, also, contain notable quantities of tannin, especially oaks, pines, elms, and willows. The sumach, the plum, the poplar, the horse-chestnut, and the elder contain tannin in the young twigs as well as in the bark. These vegetable matters also contain extractives that affect the colour of the ink. Some of them give a green ink with ferrous sulphate, some a brown, and many a purple. For ink-making purposes such dark colouring matters are required as will make what the dyers call lakes.

If a solution of alum is added to certain vegetable decoctions the colour of the solution changes, and if caustic potash or ammonia is then added we get a precipitate of coloured alumina, which is called a lake. In ink manufacture this lake is not, of course, to be produced in the ink itself. The flocculent precipitate would not remain in suspension. It is a question of having the lake in solution, which is effected by having free acid present. On writing with an ink so made, it will be seen that the writing gradually darkens. The ammonia in the air and the traces of lime in the paper co-operate to precipitate the lake, and thus make the writing more distinct.

The amount of alum to be used can be only known by experience, as it depends upon the nature and the degree of concentration of the decoction. The nature of the decoction depends, too, not only on the plant it was obtained from, but on the age of the plant and the time of year at which it was gathered. When once the right proportion has been found, the addition of ferrous sulphate will produce an ink of a particular colour, and indigo-carmine is an excellent means of bringing that colour to black, blue, or violet, as may be required. Gum arabic or dextrin is used as a thickening agent, and a little antiseptic, such as carbolic acid, is also added, as these inks are very liable to go mouldy.

Although it is impossible to give recipes for all the substances that can be used for ink making, a sufficient number are appended to act as a guide to the manufacturer.

ELDER INK.

The berries of the common elder (*Sambucus niger*) contain a large quantity of a reddish-blue dye, and give a capital ink. The writing is at first violet, but soon turns to a deep black,

Elder berries	100
Ferrous sulphate	5
Alum	2
Vinegar	5

Crush out the juice of the ripe berries and mix it with the vinegar. Then add the alum and the iron salt dissolved in hot water.

Sloe Ink.

Sloes	200
Ferrous sulphate	10
Alum	4
Vinegar	50
Water	125

Crush the unripe berries and boil them in the water. Strain, and add first the vinegar and then the alum and the copperas, both dissolved in a little hot water. A little carbolic acid is added to all these inks.

Chestnut Ink.

The prickly shells of the fruits of the horse-chestnut (*Æsculus hypocastanum*) give, with boiling water, an excellent extract for ink making.

Green chestnut shells	400
Ferrous sulphate	4
Alum	2
Water	2000

Boil the shells for a few hours in the water, strain, and add the alum and the vitriol. The bark of the young twigs of the horse-chestnut can also be used instead of the fruit.

Cutch Ink.

Cutch	10
Ferrous sulphate	10
Gum	2
Water	100

Dissolve the cutch in the water boiling, let the solution clear, decant it, and add the iron. In this way a splendid ink can be very quickly made. A small percentage of strong vinegar is a great improvement.

Walnut Ink.

The pulp of the fruit of the walnut (*Juglans regia*) con tains an extractive which quickly turns brown on exposure to the air, and is sometimes used to dye the skin a deep brown. This pulp gives a very durable ink of a fine black colour.

Green walnuts	200
Ferrous sulphate	8
Alum	2
Water	800

X.

LOGWOOD TANNIN INKS.

Logwood or Campeachy Wood.

Logwood is a medium-sized tree, indigenous to the West Indies and the greater part of tropical America, and known by the name of *Hæmatoxylon campechianum*. The wood is red or dark brown, from the presence of a special colouring matter called hæmatoxylin, which is extracted by boiling water.

The decoction is dark red, and gives an intense dark blue-black coloration with iron salts. Hæmatoxylin has a great affinity for ammonia, and forms with it crystals that are green to reflected, and red to transmitted light.

Logwood comes upon the market in fairly large pieces, sometimes with the white sapwood still adhering to it, but sometimes freed from it. It is very easy to extract the colouring matter from ground logwood, and this is therefore preferred by ink makers; but wrongly, as it is so extensively adulterated with foreign woods and water that it can only be safely bought by an expert.

Logwood Extract.

This can be highly recommended for use by the ink manufacturer, as it is very convenient, and its relative price is very small when we consider that the trouble and expense of preparing it are avoided. It can be roughly estimated that the extract is equivalent to four times its weight of the wood.

Commercial logwood extract occurs in the form of irregular pieces or flat plates with a shining dark brown surface, and readily soluble in water, leaving, if the extract is good, very little residue, which consists of substances coagulated by the heat of the evaporation.

Although logwood decoction or a solution of the extract will make ink with an iron salt and without any third substance, yet logwood is preferably used as an addition to tannin inks which are not black enough without it.

The logwood may either be boiled or macerated with the galls, or the two decoctions may be made separately and then mixed. If logwood extract is used, it is dissolved in the least possible quantity of hot water, and added to the solution of the other ingredients separately made.

The logwood tannin inks have a splendid blue-black colour and flow fairly freely. They also have the great advantage that they attack the nibs less than pure tannin inks, as the logwood probably forms a varnish on the pen when it is laid aside, which excludes the air and prevents rust.

Campeachy Ink.

Galls	9
Ferrous sulphate	9
Logwood shavings	9
Gum	9
Water	180
Vinegar	180

Dissolve the gum, the vitriol, and the galls in the vinegar, and make a decoction with the logwood and the water. Then mix. The water that evaporates during the making of the logwood decoction must be replaced.

Campeachy Extract Ink.

Galls	36
Ferrous sulphate	36
Logwood	9
Gum	36
Water	300
Vinegar	60

Proceed as above, and filter the finished ink.

Ribaucourt's Campeachy Ink.

Galls	16
Logwood raspings	8
Ferrous sulphate	8
Copper sulphate	2
Gum	6
Sugar	2
Water	200

The logwood is boiled with the water till half the liquid is evaporated. The decoction is filtered hot, and the other ingredients are dissolved in it. As soon as ink is cleared, which takes about three days, it is run off from the sediment and bottled.

Campeachy Gallic Acid Inks.

These much resemble the inks last described, and practically the only difference is that they contain gallic acid instead of gallotannin.

First Quality.

Galls	20
Logwood	30
Ferrous sulphate	20
Gum	30
Water	130

Crush the galls, and let them ferment with 80 parts of the water for a fortnight. Then draw off the liquid, and rinse the residue with enough water to dilute the liquid and washings to 100 parts. The remaining 50 of the 130 parts of water are boiled on the logwood raspings till the solution only weighs 30 parts. It is then filtered hot, and the copperas and gum are dissolved in it, after which it is mixed with the gallic acid solution. In a few days there will be a considerable precipitate. The supernatant liquid is an excellent ink of a pure black colour.

Hæmatoxylin Ink.

This differs from the last chiefly in name. The following is the recipe :—

Galls	40
Logwood	50
Ferrous sulphate	30
Gum	25
Water	200

Leave the powdered galls with part of the water for at least three months in a uniformly warm room.

The author differs here from the recipe, for a fortnight is certainly ample for the complete conversion of the gallotannin into gallic acid. If a longer time is allowed other changes set in, and the gallic acid is itself altered and much of it converted into substances quite useless for ink making. This is quite irrespective of the waste of time and capital involved in substituting thirteen weeks for two. Even if there were a little gallotannin left, that would not matter in the least. The logwood is then boiled for some hours with the gallic acid solution, water being added so as to keep the volume constant. The copperas and gum are dissolved in a little of the liquid, which is then added to the main mass.

English Logwood Ink.

Galls	100
Logwood	120
Ferrous sulphate	35
Gum	100
Vinegar	400
Water	500

This ink is made by putting all the ingredients into a vat and stirring them every day for about a fortnight. The ink will then be deep black, and can be bottled. The residue of galls and logwood is then treated with—

Ferrous sulphate	15
Gum	30
Vinegar	100
Water	150

and gives a second lot of ink of good second quality. Even a third lot of ink may be obtained by adding half the quantities last mentioned to the residue after the second ink has been drawn off.

A better plan, however, is to put the solid ingredients into a bag, which is hung, two-thirds immersed, in the vinegar and water. This gives an ink that requires no filtering. A wooden ring round the mouth of the bag greatly facilitates the filling and emptying.

The only drawback to this very convenient way of making ink is the liability of the liquid to become mouldy. It is therefore advisable to substitute crude pyroligneous acid (which contains carbolic acid) for the vinegar, or if vinegar is used, to add a little carbolic acid.

If it is desired to prepare these inks in a few hours, the bag should be steeped in the boiling liquid ingredients; the galls should be well crushed, and the logwood used either in the form of extract or of sawdust or very thin shavings.

French Logwood Ink.

Galls	55
Logwood	30
Ferrous sulphate	30
Cupric sulphate	8
Alum	2
Gum	20
Water	1500

Boil the crushed galls and the logwood shavings in the water till the liquid is evaporated to about half. Then strain the boiling liquid, and stir in the gum and the metallic salts in the state of fine powder. The ink is now fit for use, but it is better to allow it to settle for a few days. The sediment is added to the residue remaining from the first decoction, and mixed with—

Ferrous sulphate	10
Copper sulphate	2
Gum	8
Water	500

The mixture is boiled for two hours, and strained boiling hot. A second lot of ink is thus obtained, which, although inferior to the first, is better than many common gall inks. It shares with all logwood inks the manifest advantage of containing no free acid, so that it does not injure the nibs. A nib which had been used for this ink till the point had become so worn by friction that it was impossible to make a fine stroke with it appeared, when cleaned with water, perfectly polished, and showed no signs of corrosion.

Germania Ink.

Galls	200
Logwood extract	30
Ferrous sulphate	60
Alum	4
Vinegar	10
Carbolic acid	2
Water	2400

The powdered galls are mixed with 2000 parts of the water, and left in a covered vessel for fourteen days. In the meantime the logwood extract is dissolved in 200 parts of the water, and the metallic salts in the remaining 200. When the gall infusion is drawn off—it is usually very mouldy—it is mixed with the vinegar and the carbolic acid, and finally with the solution of copperas and alum. The result is an ink of the very deepest colour, which flows freely and penetrates the paper well. It resists chemicals strongly, and is very suitable for important documents which have to be preserved for long periods.

Gallic Acid and Logwood Inks.

Although the Germania ink just described is partly a gallic acid ink, as the gall decoction is used in a mouldy state, the process can be also so managed that an ink is obtained which unites the advantages of a good alizarine ink with those of a logwood ink. The following is the recipe for securing this result :—

Galls	200
Ferrous sulphate	60
Vinegar	1600
Carbolic acid	2

The galls are soaked with part of the water and left to ferment for three weeks. At the end of this time all the gallotannin will have become gallic acid. The vinegar is then added, and the liquid is strained. The residue is rinsed with water till the liquid and washings weigh 800 parts. In a part of it 40 parts of logwood extract and 2 of alum are dissolved, and then put back with the rest. The addition of the carbolic acid finishes the ink.

As appears from the description, we get first an acid ink, which, if used at that stage, gives pale green writing which gradually turns black in the air. The addition of the logwood makes the ink write, from the first, a fine blue-black which soon becomes a deep lustrous black.

All the tannin logwood inks hitherto described have, besides great cheapness of production, the additional advantage that they penetrate the paper very deeply, a circumstance which, of course, greatly increases the durability of the writing. The author has writings done with them many years ago, some of which have been purposely stored in damp cellars. The writing is as black as ever, whilst those done with ordinary logwood inks, which have been treated in the same way for the same time, have turned distinctly brown.

XI.

IRON-GALL INKS WITH COAL TAR DYES.

INSTEAD of indigo or logwood extract coal tar dyes may also be used as the "provisional colour" for iron-gall inks, and they have the advantages of not only being available in many shades, but also of possessing great tinctorial power. Only very small quantities are required to impart an intense coloration to the ink, and no foreign substances are introduced at the same time into the ink. As an example of such ink Dieterich's *Documentary Ink* may be cited :—

A *Gall Basic Ink, No. I.*, is first made as follows : Coarsely crush 200 parts of Chinese galls, moisten them with water, and leave them for ten days at 20° to 25° C. to become mouldy ; then extract them with 400 parts of water on a steam bath for an hour, after which express the extract and treat the residue first with 400 parts, and then with 200 parts of hot water. Add to the united extracts 10 parts of glycerin (specific gravity, 1·23), 7 parts of sulphuric acid (specific gravity, 1·838), 80 parts of crystallised ferrous sulphate, and 2 parts of white bolus ground up in water ; boil for five minutes, and leave for eight days at 15° to 20° C. in an open vessel. Filter and wash the residue with sufficient water to give 1000 parts of liquid in all.

Gall Basic Ink, No. II.—Extract 200 parts of Chinese galls exactly as described above. Add to the extract

10 parts of glycerin, 3·5 parts of sulphuric acid, 7 parts of oxalic acid, 160 parts of ferrous sulphate (containing 10 per cent. of iron), and 2 parts of white bolus, ground up in water. Treat as in the case of No. I., and dilute the filtrate to 1000 parts.

To prepare the finished ink mix—

100 parts of gall basic ink, No. I.
300 ,, ,, ,, No. II.
600 ,, distilled water.
20 ,, gum arabic.
1 part of carbolic acid.

Finally add the "provisional colour," according to the initial colour desired for the ink, as follows :—

Blue-Black Inks.

4 parts phenol blue 3F.
1 part ponceau RR.
1 part aniline green D.

Red-Black Inks.

5 parts ponceau RR.
0·5 part phenol blue 3F.
0·5 ,, aniline green D.

Green-Black Inks.

5 parts aniline green D.
0·5 part phenol blue 3F.
0·5 ,, ponceau RR.

Initially Black Inks.

2 parts aniline green D.
2 ,, ponceau RR.
2 ,, phenol blue 3F.

German dyeworks produce the following dyestuffs as "provisional colouring" matters for iron-gall inks :—

Black.—Echt blue, Induline, Nigrosine, Coupier's blue (all soluble in water), Deep black, Aniline black.

Blue.—Concentrated cotton blue, Pure blue, China blue, Soluble blue, Marine blue V., Paper blue, Ketone blue, Patent blue.

Green.—Acid green, Naphthalin green.

Buchheister's Writing Ink.

Tannic acid (gallotannin)	40
Copperas	20
Gum arabic	5
Oxalic acid	0·5
Citric acid	0·5
Aniline blue	2·5
Carbolic acid	1
Water	1000

In this ink pyroligneous acid, which is otherwise used, is replaced by oxalic and citric acids, and the ink is accordingly odourless.

Schluttig and Neumann's Ink.

Tannin extract, with 3 per cent. of tannin	959·66
Copperas	20·00
Gum arabic	10·00
Hydrochloric acid (specific gravity, 1·18)	7·14
Aniline dye, blue	2·20

XII.

CHROME LOGWOOD AND ALUM LOGWOOD INKS.

THE colouring matter of logwood is soluble in water and shows several very characteristic reactions. A decoction or an aqueous infusion made at ordinary temperatures is red, but alkalies turn it blue. The pure colouring matter is called hæmatoxylin, and forms yellow crystals. When the wood is exposed to the air the hæmatoxylin changes into hæmatein, which is red.

Hæmatein gives a violet compound with ammonia. Treated with solution of alum or lead acetate, and then with ammonia, it gives a blue or violet lake.

The most important property of logwood decoction for the manufacture of ink is that of forming very dark liquids with neutral chromates. These liquids can be used as inks or dyes, or for painting. On this account logwood and its extract are much used by ink makers, and rightly so, for the inks so made have a fine colour, are very durable, and cost little to make.

LOGWOOD CHROME INK.

So far only inks owing their colour to a very finely divided black precipitate suspended in a colourless solution, or those in which the black is in solution in an acid, have been described. In reality, however, none of these inks consists of a black solution which would give no sediment on standing. Such a solution, however, exists without any suspended matter whatever. It was discovered by Runge, who found that *neutral* chromates give with infusion of logwood a very black, clear liquid.

Runge found that the best salt for the purpose was the yellow potassium chromate (K_2CrO_4). Although it is not a rare salt, it is sold at a relatively high price, and the ink-maker who uses it in large quantities will find it advantageous to make it himself by the following process :—

Preparation of Potassium Chromate.

Dissolve commercial potassium dichromate in ten times its weight of water, boil, and add powdered potassium carbonate till all effervescence ceases. A slight excess of the carbonate does no harm. The liquid during the process gradually changes from red to yellow. It is then evaporated to about half its bulk in a stoneware dish, and allowed to cool, with constant stirring. The chromate then crystallises out in small yellow crystals. The mother liquor is poured off, and the crystals are dried on blotting-paper. The mother liquor can be used instead of water to dissolve a fresh lot of dichromate.

In the dichromate half the chromic acid is less firmly combined than in the other half. This seems to be the reason why an ink made with it has the drawback of changing its pure black colour to brown with time, a change probably due to half of the chromic acid having been set free. If the monochromate is used the black does not change. We do not at present know the nature of the reaction between logwood dye and monochromate. Some chemists think that the chromium combines with the dyestuff. Although various compounds of organic dyestuffs with metallic oxides are known, in the author's opinion there is not much foundation for this opinion, for a very small amount of potassium chromate will convert a large quantity of logwood infusion into ink, and the proportion of chromium to hæmatein present is so insignificant that it seems unlikely that there is combination between the two, although it is, of course, possible. The amount of monochromate required to convert a given quantity of infusion into ink varies greatly, probably on account of the variable amounts of colouring matter present in different kinds of logwood. Moreover, it is of great importance to take just the right quantity of chromate. If too little is used, the colour is not full enough, and if too much, the black, although satisfactory at first, will turn brown like that obtained with dichromate. Although it is impossible to give the exact proportions for all kinds of logwood, yet it will be found that a solution of 2 lb. of chromate in 2 gallons of water, when added to a decoction of 40 lb. of logwood in 24 gallons of water, will always give a satisfactory ink.

The finely divided logwood is boiled with the water till the solution has evaporated to about 20 gallons. The decoction is then strained, and the chromate solution is added in very small portions, with constant stirring. After a time a sample should be taken. If it is transparent and writes red or violet, more chromate is wanted. Enough has been added when the liquid is black and writes a blue-black. The quantities used and the brand of the logwood should be noted for future reference.

Logwood Extract Chrome Ink.

It is simpler and better to use the extract than logwood itself.

Logwood extract	2,000
Potassium chromate	10
Water	100,000

Dissolve the chromate in the water, and hang the extract in a bag in the solution.

These logwood inks are all very cheap, very black, and very durable. They penetrate the paper very deeply, and after a few days the writing will offer great resistance to chemicals.

Violet Logwood Ink.

Logwood	100
Alum	5
Gum	10
Water	500

Boil the logwood with the water, dissolve the gum in the hot decoction, and finally add the alum previously dissolved in a little hot water. If a more purple shade is desired, reduce the alum to two-thirds or a half of the above quantity. If, however, the ink is to be blue-black with a violet tinge, add carefully a solution of chromate till the wished-for colour is reached.

Free-Flowing Logwood Ink.

Solution of logwood extract	440
Dextrin	80
Water	1080
Alum	72
Sulphuric acid	6
Potassium chromate	3

The sulphuric acid is added before the chromate and the alum.

Ordinary Logwood Ink.

Logwood extract	1110
Dextrin	30
Alum	600
Water	80,000

To the solution of the extract add first the alum and then the dextrin. The alum is hung in the solution in a bag till it is all dissolved.

Violet Logwood Ink.

Solution of logwood extract	300
Alum	12
Dextrin	15

The alum is dissolved by heating it in part of the extract solution. Finally, one and a half parts of finely powdered acetate of copper are hung in the ink in a bag.

Red Logwood Ink.

Solution of logwood extract	50,000
Dextrin	2,500
Alum	2,500
Acetate of copper	20

The finished ink is carefully reddened with small additions of sulphuric acid, being stirred vigorously each time. This ink does not attack steel nibs so much as might have been expected, especially if the ink is allowed to dry on the pen after the first using.

Dieterich's Imperial Ink.

(1) Logwood extract (200 parts French extract, 1000 water) . . . 200

(2) Water heated to 90° C., and treated, drop by drop, with—

Potassium dichromate	2	500
Chrome alum	50	
Oxalic acid	10	
Water	150	

The mixture is heated at 90° C. for thirty minutes, and diluted to 1000 parts with water.

Finally, 15 parts of gum arabic and 1 part of carbolic acid (or salicylic acid) are added.

XIII.

COPYING INKS.

It is unnecessary to enlarge upon the importance of copying inks, especially as copying inks can now be made that require no press or any other mechanical contrivance.

The essential feature of a copying ink is to dry slowly, so that the writing may be copied even after a considerable interval. This property is given by mixing the ink with hygroscopic substances, that is to say, such substances as keep moist by absorbing water from the atmosphere. The hygroscopic bodies which we use are sugar, glucose, dextrin, glycerin, or calcium chloride. The hygroscopicity of the last substance is so great that it has to be used in very small quantities. Excess of any of these substances causes the writing to remain too damp and liable to be effaced.

Any of the inks already spoken of can be made into a copying ink by adding it to the proper quantities of thickening and hygroscopic substances, but inks in which there is a suspended precipitate are less suitable for copying inks than those in which the colouring matter is in solution. The reason of this is that the latter inks penetrate the paper more deeply than the former, and hence remain copyable longer than inks in which only the liquid parts penetrate and the coloured precipitate remains upon the surface, where it is only retained by the thickening substance.

A very simple experiment will convince anybody how different the precipitate-containing inks are from the others. The dry writing of one of the former can be washed away to a large extent with a damp sponge two or three hours afterwards, and even made quite illegible. This is quite impossible when the ink used had its colouring matter in solution.

A copying ink with a suspended colouring matter will generally give one copy only, and that a bad one, while the original will be nearly obliterated. When, on the other hand, a copying ink has its colour in solution, the pigment penetrates the paper, and hence the characters consist of liquid of a particular depth. The lowest part of it adheres so firmly to the paper by capillary attraction that it cannot be removed. The surface of the paper may, however, be likened to a soaked sponge, for when another porous body is pressed on to it, it gives up to it part of the liquid it contains, and gives a sharp copy without injuring the original. When the copy is removed there is enough liquid left to give, with a somewhat stronger pressure, a second copy as sharp as the first. By the use of moistened paper and a still greater pressure a third or even a fourth copy can be taken from the same original. The amount of pressure and its duration must be greater for each successive copy, and the pressure is best applied with a copying press.

The paper to be used for taking copies must be unsized and of a high degree of porosity, so as to suck up the ink freely. It must also be so thin that the copy penetrates it through and through. It is often necessary to hold the copy up to the light before it can be read, especially if it is the third or the fourth copy. These are always pale, even when a very good copying ink is used. It is a good plan to keep the copying paper in a tin box with a small vessel of water. This will keep it damp, and it will then take more copies than a perfectly dry paper, even with a moderate pressure.

Principle of the Copying Press.

Although the copying press is being rapidly superseded by the process of typing duplication, it is still required for taking copies of written documents. In the earliest forms of presses strong wooden boards covered with several layers of soft paper were used to obtain the pressure, but in the modern forms iron is used instead, and the pressure is applied by means of a screw instead of a lever, and the paper coating of the plates is replaced by india-rubber.

The writing to be copied is laid on the lower plate, and covered with the copying paper, and this with blotting-paper. The upper plate is then brought down upon the three. The amount of pressure required depends on three factors—the nature of the ink, the time that has elapsed since the original was written, and the degree of dampness of the copying paper. The more deeply the ink of the original has penetrated the paper, the fresher will be the characters; and the nearer the paper is to the right degree of dampness, the less will be the pressure wanted, the sharper the copies, and the larger the number obtainable. The pressure causes the copying paper to take up a part of the ink from the original, and the copy is visible on both sides of the paper. Care must be taken in removing the copy, which will, of course, adhere to the original to some extent.

If more copies than one are wanted, the others should be taken as quickly as possible after the first. The longer the time, the more the ink of the original dries and the less distinct does the copy become.

It is possible to obtain copies, if the original is damped on the back by means of a wet sponge, long after it has become impracticable to get any without resorting to this device. The moisture, of course, soaks through the paper to the ink on the other side and brings it back, at least in part, to the liquid form, when sufficient pressure, after the water has been allowed time to act, will often result in the production of one perfectly good copy at least.

Single Iron-Gall Copying Ink.

Galls	120
Ferrous sulphate	30
Gum	20
Glucose	10
Water	1000

Here the glucose is the hygroscopic agent. As it easily ferments, whereby the ink would be spoiled, some carbolic acid must also be added. If the ink is found to be too sticky, it should be mixed with some that has been made without either gum or glucose.

Double Iron-Gall Copying Ink.

Galls	7
Ferrous sulphate	7
Logwood	16
Gum	5
Glucose	2
Water	60
Vinegar	10

The logwood may be replaced by about one-tenth of its weight of logwood extract. A little more does no harm, as it is itself hygroscopic and hence contributes to the copying properties.

Dieterich's Iron-Gall Copying Ink.

Iron-gall basic ink, No. I (see p. 66)	700
,, ,, No. II. (see p. 66)	100
Distilled water	200
Glycerin (specific gravity, 1·23)	4
Gum arabic	20
Carbolic acid	1

The ink is coloured as desired by means of the dyestuffs mentioned on page 67.

Buchheister's Iron-Gall Copying Ink.

I.	Tannin	45	dissolved in warm water, 540.
	Tannin extract	45	
II.	Ferrous sulphate	60	in water, 400.
	Pyroligneous acid	5	
	Sulphuric acid	4	

The two solutions are mixed, and coloured with aniline blue (10 parts) for blue, nigrosine (20 parts) for black, or Ponceau (10 parts) for red.

Logwood Copying Ink.

Logwood extract	100
Ferrous sulphate	2
Copper sulphate	1
Alum	12
Glucose	8
Potassium chromate	1
Indigo carmine	19
Water	500

The logwood extract, glucose and indigo carmine are dissolved in 400 parts of water, and the salts in the remaining 100 parts, and the two solutions are mixed and thoroughly stirred.

Glycerin Copying Ink.

Logwood extract	200
Ferrous sulphate	8
Potassium chromate	2
Indigo carmine	16
Glycerin	20
Water	1000

This excellent ink is made by dissolving the extract, the iron salt, and the chromate simultaneously in the water, and then adding the glycerin and the indigo carmine. The glycerin does not thicken the ink very much, and the ink therefore flows freely enough for the finest hair strokes to be made with it. Yet, even with this great advantage the ink will give many copies, as it dries very slowly and penetrates the paper very deeply.

Böttger's Copying Ink.

Logwood extract	64
Sodium carbonate	16
Potassium chromate	2
Glycerin	64
Gum	16
Water	270

Dissolve the sodium carbonate and the extract together in the water, then add the gum and the glycerin, and lastly the chromate dissolved in the smallest possible quantity of hot water. The ink is then ready for immediate use. This ink will give three copies merely with the pressure of the hand, and two more afterwards in the press.

Logwood Copying Ink.

Logwood extract	70
Vinegar	1000
Water	1000
Ferrous sulphate	40
Alum	20
Gum	35
Sugar	60
Glycerin	4 to 6

Buchheister's Logwood Copying Ink.

Logwood extract	50
Oxalic acid	6
Alum	35
Glycerin	10
Pyroligneous acid	60
Water	1000

The logwood extract, oxalic acid and alum are dissolved in the water, and the glycerin added to the solution, which is then allowed to settle. It is next boiled, the pyroligneous acid added, and the ink once more clarified by standing.

Birmingham Copying Ink.

Logwood extract solution	5200
Dextrin	240
Alum	265
Verdigris	2
Oxalic acid	16
Glycerin	56-168

The amount of glycerin to be used depends upon the time during which the ink is to remain copyable after writing.

Allfield's Copying Ink.

This is intended for use without a press. It is made by evaporating 10 gallons of ordinary iron-gall ink down to 6, and then making up to the original volume with glycerin. The copying is done by mere contact of the copying paper, but the writing is very easily smudged.

Dieterich's Blue Copying Ink.

Resorcin blue	10
Distilled water	950
Sugar	10
Oxalic acid	2

Dieterich's Red Copying Ink.

Eosine A	25
Sugar	30
Distilled water	1000

Additional recipes for coloured copying inks are given in the chapter on coloured inks.

KNAFFL'S COPYING INK.

The following preparation is of the greatest value to architects and engineers, as it gives two or three copies without any wetting of the paper, and of such sharpness that the finest lines of the original are faithfully reproduced. It is rather expensive, but that is of minor importance, as its use saves all the great time and labour involved in making a copy of a plan or working drawing by hand.

Solution of pyrogallol	240
Copper sulphate	4
Iron chloride	10
Uranium acetate	2

Pyrogallol is now so much used in photography that it can be bought fairly cheaply. The uranium acetate is dearer, but since uranium compounds have come into use for black painting on porcelain their price has fallen considerably. The iron chloride is easily made by saturating 10 lb. of commercial hydrochloric acid with iron, adding 1 lb. of strong nitric acid, and evaporating till crystallisation begins.

To copy a drawing made with this ink a sheet of thick, well-glazed paper is laid on the original (Bristol board answers excellently), and then a smooth board, and the whole is uniformly weighted, but not excessively, with books. In from three to five days the copy will be ready. Since the invention of hektographs, chromographs, opalgraphs, etc., and the development of the stencil process for duplicating typewritten documents, copying inks have lost part of their importance in certain directions. By the use of these different forms of apparatus, with suitable inks, we can obtain not merely two or three copies, but sixty or even one hundred copies.

Valuable as are these duplicating methods when a large number of copies is required, they will never cause the ordinary copying process as described above to be altogether abandoned, since, notwithstanding the almost universal adoption of the typewriter, many documents have still to bc written by hand.

XIV

COAL TAR DYES AS WRITING INKS.

In the absence of certain chemicals, especially iron and copper compounds and acids, that are needed for the manufacture of the best qualities of ink, intended to answer to every requirement, inks may be prepared from coal tar dyes, which are quite suitable for writing letters, etc., for which no degree of permanence is expected, and which are not intended to offer any resistance to chemicals. Their preparation is very simple, for they consist of nothing more than water, the appropriate dyestuff, and a thickening agent such as gum arabic or other vegetable gum. Owing to their intense tinctorial power only very small amounts of the coal tar dyes are needed for making an ink, and a 5 per cent. solution will give writing that is reasonably fast to light under the ordinary conditions of use, and which, if kept in the dark, will retain its original intensity of colour for a long time. Another advantage of these inks is that they do not thicken or decompose when the water evaporates from them on standing, and may be reproduced in their original condition by the addition of more water.

The following dyes *inter alia* are suitable for making bright-coloured inks: Eosine extra AG, extra 2A, eosine yellow S, eosine extra conc.; rhodamine O, rhodamine extra, rhodamine B, rhodamine extra B; fuchsine (magenta) extra yellow, extra yellow small crystals, and fuchsine-double-refined; new fuchsine, methyl-violet (all brands), malachite green crystals extra, brilliant green extra crystals ; patent blue L, V, A, and AGL, ink blue 3G, 2G, G, acid green conc. M, and conc. O, naphthalin green V conc. *For Black.*—Carbon black O, I, II, 6618 ; wool printing black NB ; carbon black GA ; and nigrosine, Nos. 1 and 4, all being products of the firm formerly known as Meister Lucius and Brüning. It is also possible by combining red, yellow, and blue dyes to prepare fairly deep black, although not absolutely black inks.

To make these inks about 5 per cent. of the dye is dissolved in warm, not hot, water, in which about 5 per cent. of gum arabic has previously been dissolved, and the solution is stirred and filtered from any impurities that may be present.

XV.

HEKTOGRAPHS.

THE subject of hektography may conveniently be dealt with in three sections—the preparation of the hektograph, the manufacture of the ink, and the making of the copies.

If a solution of glue that has been boiled down till it would set to a firm mass if allowed to cool is mixed with a certain amount of glycerin, it will then set, indeed, but will remain permanently sticky and very elastic. This property of a mixture of glue and glycerin has caused it to be used for years for the rollers of printing machines.

If one pours the glue and glycerin mass into a flat plate with an edge, and writes on paper with a very thick-flowing ink containing a very powerful colouring matter, such as an aniline dye, either dissolved or in solution, and also glycerin, and then lays the paper, writing downwards, on the gelatin mass with gentle pressure, a large part of the ink will be retained by the gelatin, which will therefore show a reversed copy when the original is taken off. If the original is then replaced by a blank sheet of paper, a moderate hand-pressure will convert it into an exact copy of the original, and in this way from 60 to 100 copies can be successively obtained. To prepare the gelatin for a fresh writing the old one must be erased with a damp sponge, which removes the upper part of the preparation together with the ink in it. The rest can be used again as soon as it is dry. The "graph" is kept shut up when not in use to prevent its surface from becoming contaminated with dust.

The Preparation of Hektograph Compositions.

A very simple and yet very good method is to take glue of good quality—it is quite superfluous to use gelatin for this purpose—and to soak it in cold water for twenty-four hours. When taken out it will be much swollen, and it is then melted in an enamelled pot over a gentle fire. When all the glue is quite liquid, the glycerin is added and mixed with it perfectly by careful stirring. The mixture is kept hot till it flows thinly, and so that all the bubbles produced by the stirring may rise to the surface and break. Any scum that may rise is carefully removed with a shallow spoon. The mass is then cast into plates.

The only way to tell whether the preparation is of the right consistence is to take copies with it. If it contains too little water through overheating, and is therefore deficient in elasticity and stickiness, the ink will only give a few copies. This fault is corrected by stirring hot water into the composition. If, on the other hand, it has not been evaporated enough, it will be very elastic and so sticky that the paper can only be taken off it with great difficulty, and the copies will smudge and be indistinct. In this case, of course, the mass must be concentrated by further heating.

Many recipes direct the addition of white powder—a mineral such as kaolin, chalk, or zinc white—to the glue and glycerin. The object of these is simply to whiten the mass and make the reversed copy more distinct.

Recipes for Hektographs.

Simple "Graphs."

A.

Glue	100
Glycerin, 28° B.	500

B.

Glue	100
Glycerin, 28° B.	400
Water	200

Mix the glue and glycerin as above described.

CHROMOGRAPHS.

The ink written on a hektograph can be more easily removed after use if inactive bodies are added in the form of fine powder. One of the best to use is sulphate of barium. To prepare this, precipitate a solution of chloride of barium with sulphuric acid, and wash the precipitate repeatedly with water, pouring off each lot of water when the white sulphate has settled to the bottom. The sulphate is used after the last washing in the form of a thin paste.

A.

Glue	100 grammes.
Barium paste	½ litre.
Dextrin	100 grammes.
Glycerin	1000-1200 „

The mass is warmed and stirred till all the glue and dextrin are dissolved, and then poured into the plate. Test a sample of the mass by copying from it as above directed (p. 85).

B.

Glue	100 grammes.
Barium paste	½ litre.
Glycerin	1200 grammes.

C.

(*Recommended by the French Ministry of Public Works.*)

Glue	100
Glycerin	500
Finely powdered heavy spar or levigated kaolin pipe-clay	25
Water	375

To avoid this washing of the surface of the mass hektograph leaves are also made. For this purpose the liquid composition is poured on to a polished sheet of glass kept truly horizontal, and is then transferred, before setting, to a sheet of porous paper, which is pressed down upon it, care being taken to prevent the formation of air bubbles. The paper and adherent film of composition are then separated from the glass. The surface of these hektograph leaves is very smooth, and particularly suitable for taking copies of drawings, etc.

As ink for this chromograph a concentrated solution of aniline violet is recommended.

In the author's opinion the simple hektographs are the best. By varying the proportions of glue and glycerin the number of copies procurable can be regulated as desired, as also the readiness with which the writing can be separated from the mass.

XVI.

HEKTOGRAPH INKS.

As already mentioned, the function of a hektograph ink is in the first place to adhere to the composition and to be gradually transferred to the copies. The copies get fainter and fainter until, when the retentive power of the gelatin becomes equal to the absorptive power of the paper, the copying comes to an end, although the writing is still distinct upon the gelatin. Obviously one of the first requisites for a hektograph ink is that it should contain a very deep and powerful dye and enough glycerin to make it resemble a very slowly drying copying ink.

Of all known colouring matters the aniline dyes have the greatest tinctorial power, and hence they alone are used in the manufacture of hektograph inks. Many of those at present on the market are not particularly satisfactory products. They do not flow freely enough for use with the pen. The chief reason of this is that most of the aniline dyes require alcohol to make strong solutions of them, and in use the alcohol evaporates so fast that the ink becomes thick before the pen is empty.

There are, nevertheless, aniline dyes which are sufficiently soluble in water, and among them we have blues and reds that make excellent ink. There is no difficulty in writing with them, and, in fact, only water-soluble aniline dyes should be used for hektograph inks. We can, however, adopt the device of incorporating aniline dyes that are insoluble in water with the inks with the use of so little spirit that the ink does not dry too fast. The process is as follows :—

The dye is mixed with the weighed proportion of glycerin in a porcelain mortar, and after being heated at 40° to 50° C. they are ground up together. The coal-tar colours are soluble in glycerin, especially with the aid of heat. If the mass is too viscid, it is diluted with hot water to the consistence of a syrup. When no more solid particles can be felt with the pestle the dye can be brought perfectly into solution by carefully adding about 50 per cent. of alcohol. By this method very good hektograph inks can be obtained, even with methyl violets insoluble in water.

Blue Hektograph Inks.

Lehner's Recipe.

Water-soluble blue	10
Glycerin	10
Water	50-100

Mix with the aid of gentle heat. The amount of water should be taken between the limits stated according to the number of copies required. This ink will be found excellent for every requirement, and will copy the finest strokes perfectly.

Methyl Violet Inks.

A.

Methyl violet	10
Dilute acetic acid	5
90 per cent. alcohol	10
Water	10
Glycerin	5

B.

Methyl violet	10
Alcohol	10
Gum	10
Water	70

The ingredients are kept together for about two hours at 50° to 60° C., and then filtered hot through flannel.

Red Hektograph Inks.

A.

Diamond magenta	20
Alcohol	20
Acetic acid	5
Gum	20
Water	140

B.

Diamond magenta	10
Alcohol	10
Glycerin	10
Water	50

These inks are prepared in the same way as those with methyl violet. The second recipe gives a very good ink.

Violet Hektograph Inks.

Any shade of violet can be obtained by mixing blue and red inks in different proportions. Specially serviceable in this connection are the blue inks made with water-soluble blue and the red ink last given.

Green Hektograph Ink.

Water-soluble blue	10
Picric acid	10
Alcohol (per cent.)	30
Glycerin	10
Water	30

Different shades can be made by varying the amount of picric acid.

Black Hektograph Inks.

Aniline black or nigrosine is insoluble in water, and black hektograph inks are prepared by grinding up a mixture of a very dark methyl violet and nigrosine with alcohol and glycerin.

Methyl violet	10
Nigrosine	20
Alcohol	60
Glycerin	30
Gum	5

Buchheister's Black Hektograph Ink.

Nigrosine	15
Spirit	40
Glycerin	100
Acetic acid	5
Water	500

The following dyes are recommended for use in the manufacture of these inks :—

Violet	Methyl violet and crystal violet.
Green	Brilliant green and malachite green.
Red	Fuchsine.
Yellow	Auramine.

Further reference to these dyes will be made in the section on coloured inks.

XVII.

INKS FOR TYPEWRITERS.

In the modern typewriter the levers, on the ends of which the letters are cut, are brought by the depression of the keys into contact either with a travelling inked band (the ribbon) or with a pad saturated with the ink, which is then transferred to the paper in a manner analogous to that effected by a metal stamp.

In order that an even impression may be obtained, it is necessary for the ribbon to be uniformly saturated with a strong solution of the dyestuff and to remain permanently moist. Hence many of the inks made for the purpose closely resemble hektograph inks, although the modern preparations are more akin to printing inks.

The oldest method of preparing these inks was to grind up the colour with glycerin, and ink made in this way has long been used for saturating typewriter ribbons.

Walther (*Chem. Zeit.*, 1921, pp. 169-171) gives the following requirements for typewriter inks: They must not attack the metal type (this excludes the use of acids and alkalies); they must not clog the type; and (the main essential) they must produce good impressions.

With regard to the preparation of these inks the same chemist observes: Formerly typewriter inks consisted of solutions of aniline dyes and glycerin. They gave good clear impressions, that could be copied, but in time the glycerin absorbed moisture and the impression became blurred. Then oil-soluble dyes were used for the purpose, dissolved in warm oleic acid with the addition of acid-free paraffin wax or mineral oil. The pigments used for the black inks were oil-soluble nigrosine, and Ceres dyes and the like were used for the coloured inks; but the ribbons saturated with these inks did not give copyable impressions. At the present day ground-up pigments are principally used, and these are incorporated with the medium by means of rollers. The degree of fineness required is ascertained by rubbing the pigment with the tip of the finger on paper. Lampblack is used for the black inks, and coal-tar dye lakes are the most suitable for the coloured inks, although Prussian blue, substitutes for vermilion, and the like are also used. In preparing coloured typing inks body pigments are avoided, since a mixture of dark pigments with vaseline gives black, not blue or violet, impressions. Zinc white is generally used to lighten the tints; the body pigment and additional pigment are mixed in the dry state, and the mixture is ground up with vaseline or with mineral oil. Such inks do not yield copies from the impressions. The basic dyes, such as methyl violet, methylene blue, malachite green, safranin, etc., are especially suitable for the purpose, and when finely ground up with vaseline yield an ink ready for use. The impressions are dull at first, but become sharper after copying. Castor oil and sesame oil are also used as media with which to grind the dyes.

Lehner's Typewriter Ink.

Heat pure glycerin, and add to it in small portions its own weight of water-soluble blue. On cooling, the mass becomes sandy, as part of the dye separates out again in the solid state in the form of minute crystals. Now add cautiously and with constant stirring just enough water to redissolve these, and no more. The finished ink will then be a thick bluish-black liquid. The ribbon, which is made of thin silk, is run through it, and then subjected to heavy pressure between smooth rollers. In this way a ribbon is obtained which will give a deep blue writing for many months, even with constant use.

Higgin's Typewriter Ink.

(*German patent*, 71912.)

Castor oil	4
Creosote or carbolic acid	2
Cassia oil (in the creosote)	2
Methyl violet or other aniline dye	24

Walther's Typewriter Ink.

Ten parts of finest lampblack are ground up between rollers, at least twice, with 40 parts of vaseline; 5 parts of a solution of nigrosine base in oleic acid (1 : 2) are then added, and the mixture again ground. This ink resists both mechanical and chemical attempts to erase it.

Hektograph Typewriter Ink.

Crystal violet	100
Glycerin (28° Be.)	300
Water	190
Hydrochloric acid (20°-22° Be.)	60
Dextrin solution	50

The dye is first dissolved in the warm glycerin, and the other ingredients then added with vigorous stirring.

Bersch's Typewriter Ink.

Soap	30
Glycerin	125
Water	360
Alcoholic solution of dye	721

The soap is dissolved in the glycerin, and the other ingredients added. If the ink is too thin, more soap is added.

Iron-Gall Pigments for Typewriter Ribbons, Rubber Stamps, Etc.

(German patent 229,467, E. Beyer, Chemnitz.)—In the original patent (224,637), to which the present is an addition, oil, glycerin, or an aqueous solution of shellac was mixed with the condensation products of ammonium, ammonio-ferro- or ferri-gallate (or analogous substances) with aldehydes (formaldehyde). It has now been found that the ketones, e.g., acetone, will furnish with the same complex gallates compounds suitable for making inks for typewriter ribbons, rubber stamp pads, inks of the type of Indian ink, etc. The above ammonium salt, for example, is dissolved in hot water, and acetone is stirred into the warm solution. The resulting condensation product, though soluble in water, can be precipitated by an excess of acetone, and when dried forms a deep black powder suitable for making copying inks.

Ferrogallic Inks for Rubber Stamps, etc.

(German Patent 224,637, E. Beyer, Chemnitz.)—Ammonium ammonio-oxyferrigallate (e.g., 500 parts) is dissolved in water (25,000 parts), and treated with 40 per cent. formaldehyde (1000 parts), the precipitate being then washed with water and dried at 70° C. This deep violet-black powder is perfectly insoluble in water, and is ground with oils or fats and glycerin for the production of stamping and typewriter inks. It may also be made into a kind of Indian ink by grinding it with an aqueous solution of shellac, a little coal-tar dye, lampblack, etc., being added. Other aldehydes, e.g., benzaldehyde, may be used.

XVIII.

SAFETY INKS.

CHEMISTS have long endeavoured to discover inks that are absolutely indelible except when the material written on is also destroyed. The value that such an ink would have is self-evident. Paper when properly made and kept—in air-tight boxes, for example—is so durable that we do not yet know how long it can last, and documents written on such paper with such an ink would not only resist the ravages of time for thousands of years, but would offer an insuperable barrier to falsification. Unfortunately, there is no recipe known to the author that will yield an ink capable of withstanding all exterior influences. A skilled chemist, who is prepared to devote the necessary time and care to the work, can efface inks prepared by the published recipes, and leave no trace of their former presence. It is true that free carbon bids defiance to all chemical agents and is insoluble in all the usual solvents. Ink made with any form of carbon, however, whether lampblack, gas black, soot, or charcoal, does not carry the carbon inside the paper. The black particles are simply mechanically attached to the surface, whence they can be perfectly washed off by a skilled hand. Inks of the type of printers' ink alone are exceptions. In these lampblack is mixed intimately with boiled oil, which carries the carbon into the pores of the paper. With very porous paper it is impossible with the greatest skill and patience to efface entirely the characters by any means. Unfortunately printing ink is much too thick for writing purposes.

Of all the black pigments consisting of carbon, Indian ink contains that element in the most finely divided state. Direct experiments, however, have shown that even after the lapse of years the writing done with the purest Indian ink can be removed by soaking in water and repeated delicate treatment with a soft sponge. According to the author's experience, the permanence of writing depends less upon the resisting qualities of the ink than upon the depth to which it penetrates the paper. Hence easily flowing inks used on soft porous paper will give a much more permanent writing than inks owing their colour to solid matter. Ordinary "alizarine" inks, which contain considerable amounts of indigo carmine, are very difficult to erase, and when the paper is so porous that the ink penetrates it from side to side its removal is practically impossible.

The inks which consist mainly of vegetable extractives rich in humus are of extraordinary durability. If we write with a solution of glucose mixed with 1 per cent. of caustic potash or soda, the letters are at first a pale brown, but gradually darken, and offer great resistance to acids or alkalies, and even to chlorine. The only effect, indeed, of these bodies is to set free more carbon from the humus substances, and so to increase the blackness of the writing.

There are many compositions extolled as safety inks, and some of them are fairly good, but none of those examined by the author can resist the skill of a trained chemist.

Document Safety Ink.

Ruby shellac	15
Borax	8
Gum	8
Soot	10
Water	130

The shellac is powdered and boiled with the borax and water till dissolved. The solution is filtered. In the meantime the gum and the soot are intimately mixed, put into the vessel in which the shellac was boiled, and boiled with part of the clear filtered solution. When the gum is dissolved the rest of the shellac solution is gradually stirred in. The finished ink is allowed to stand for a few days, so that the coarser particles of soot may settle to the bottom, and is then decanted or siphoned off.

Shellac-resin forms with the boric acid of the borax compounds of a dark brown colour, which resist chemical agents so well that the writing cannot be effaced completely without their effects upon the paper being clearly visible. The only object of adding the soot is to make the ink more legible, and the ink is just as permanent without it. It may be replaced by a little indigo carmine or a very concentrated chrome-logwood ink.

Read's Safety Ink.

This ink is characterised by its essential constituent being Prussian blue. It is a solution of that pigment in oxalic acid. The purest blue must be chosen, as the inferior qualities are always largely adulterated with chalk and other foreign substances.

In order that the Prussian blue may dissolve readily in the oxalic acid it must undergo a preliminary treatment. This consists in keeping it for a week in a porcelain dish with its own weight of sulphuric acid. The acid is then poured off, and the pigment is repeatedly washed by decantation with water until the wash water no longer has a sour taste. When the last lot of wash water has been drained off from the Prussian blue the wet sediment is dissolved in a solution of oxalic acid. The usual proportions are 1 lb. of oxalic acid dissolved in 5 lb. of water to every 5 lb. of Prussian blue. The resulting solution is decanted and mixed with its own volume of a good logwood-chrome ink.

Writing done with this ink penetrates very deeply, and hence is very difficult to efface.

Colophony Safety Ink.

Colophony	10
Crystalline sodium carbonate	10
Soot	2
Gum	4
Water	100

The colophony is dissolved by boiling with the water and the sodium carbonate. A clear solution is obtained more quickly if three of the 10 parts of sodium carbonate crystals are replaced by one of caustic soda. The gum and soot are mixed and stirred into the solution.

Water-Glass Ink.

This is an excellent safety ink. Baudrimont, its discoverer, made it by mixing soot with ten times its weight of potassium silicate. The potassium silicate (or sodium silicate, the ordinary water-glass) is bought in the form of a thick solution, which must be kept from the air or it will set solid, by the liberation of silica from it by the carbonic acid of the air. The soot is first mixed with a little of the water-glass by long-continued rubbing, and the paste, when quite uniform, is stirred into the rest of the silicate. The ink must be bottled up airtight as soon as it is made. When it is used the carbonic acid of the air acts upon it as above described, and the silica, enclosing carbon within it, is set free in the pores of the paper. Both the silica and the paper thus protect the carbon from mechanical removal. As, however, the potassium carbonate (or sodium carbonate) also formed might injure the paper, it should be rinsed out with weak vinegar, which, in its turn, should be removed by rinsing with water.

Carbon Safety Ink.

This is a kind of liquid Indian ink prepared from soot or lampblack.

Soot	10
Gum	10
Oxalic acid	5
Water	200

The solid ingredients are ground up with the water, which is added to them a little at a time, until there is obtained a perfectly uniform paste which can be stirred into the rest of the water. This ink, however, like all such inks, only penetrates the paper very slightly. Hence, although the carbon they contain enables them to offer successful resistance to attempts to efface them by chemical means, they can be easily and completely removed with care by mechanical processes.

Vanadium Ink.

This is one of the discoveries of Berzelius. It is prepared by adding ammonium vanadate to a filtered decoction of galls. The vanadate has a far more energetic action than that of potassium chromate or decoction of logwood. A few drops of a solution of ammonium vanadate will convert a large quantity of decoction of galls into a deep black ink, which has the advantage of flowing very freely. The ink cannot be destroyed completely by any known means; the writing always remains legible, although it becomes grey-green in time.

Lehner's Safety Ink.

Mix concentrated sulphuric acid with twenty times its weight of water, and colour the solution with a little indigo carmine or water-soluble blue. The colouring matter is added merely to make the writing visible from the first. Write with a quill on good paper. In a few days the sulphuric acid will have become strong enough, by the evaporation of the water, to carbonise the paper. As soon as the writing turns black the paper is soaked for a few days in a 5 per cent. solution of sodium carbonate, then rinsed several times with plain water and dried. The black characters will then last as long as the paper itself, and cannot be effaced. If the neutralisation with sodium carbonate is delayed, the paper will be eaten into holes by the acid, but if it is done at the right moment that will not happen.

Buchheister's Safety Ink.

Borax	30	made up to 1000.
Water	680	
Shellac	60	
Gum	30	
Aniline black	10	
Lignite extract	200	

The borax is dissolved in water and the solution boiled with the shellac and filtered; the other ingredients are dissolved in the filtrate, and the whole diluted with water to 1000 parts.

The lignite extract is made by extracting lignite with ammonia and dilute alcohol, evaporating the extract to dryness, and mixing the residue with water.

Permanent Iron-Gall and Logwood Inks.

The following recipe for the preparation of an ink that will resist changes of temperature, sunshine, and treatment with water or alcohol is given in *Chemisch-technische Industrie*: Dissolve 15 parts of tannin and 3 parts of gallic acid in 250 parts of water, and, in another vessel, dissolve 18 parts of copperas, 7 parts of gum arabic or a substitute therefor, 5 parts of hydrochloric acid, and $\frac{1}{2}$ part of carbolic acid in 200 parts of water. Mix the two clear solutions, and the ink will then be ready for writing.

For the preparation of the logwood ink, dissolve 180 parts of logwood extract or (as a substitute) of artificial indigo in 250 parts of boiling water. In another vessel dissolve 3 parts of potassium dichromate in 170 parts of water at 65° C. Mix the two solutions, stir thoroughly, and add 50 to 70 parts of hydrochloric acid. This ink yields very permanent writing.

XIX.

INK EXTRACTS AND POWDERS.

FREQUENT attempts have been made to bring inks upon the market in concentrated forms which would yield a good ink directly they were mixed with water. Although many of these preparations really give good results they are very little used, as writers will not take the trouble to make the solution.

INK EXTRACTS.

Ink extracts can be very easily made by evaporating inks to a certain concentration and then bottling them. The process, however, varies in difficulty according to whether the ink owes its colour to dissolved or suspended matter. With the latter kind it is best to concentrate the gall decoction by itself in a shallow pan, but without boiling it, down to about one-quarter of its original volume. The other ingredients are then dissolved in it. The result is a syrupy liquid which gives a good ink with from five to eight times its volume of water.

If an extract for an alizarine ink is wanted, the ink is made according to one of the above recipes, and carefully evaporated. For this purpose earthenware vessels should be used, as those of iron or copper are attacked by the acid in the ink. When, too, the ink during evaporation becomes turbid owing to loss of acetic acid, a little of the strong acid should be put in. By observing this precaution, and also by evaporating at a low temperature, the ink can be made very concentrated indeed, and can then be bottled and diluted with water for use.

Logwood-chrome inks and horse-chestnut inks can be evaporated to very thick syrups without their quality being in the least impaired or the readiness with which the extract gives an ink with water being affected.

Dieterich's Logwood Writing Ink Extract.

Logwood extract	70
Potassium dichromate	2
Chrome alum	50
Oxalic acid	10
Salicylic acid	1·5

Dieterich's Logwood Copying Ink Extract.

Logwood extract	100
Aluminium sulphate	40
Potassium oxalate	40
,, bisulphate	20
,, dichromate	3
Salicylic acid	1·5

Ink Powders.

These powders make ink when mixed with water. Most inks may be obtained in the form of powder by various simple devices.

Tannin and Gallic Acid Ink Powders.

The galls, either fermented or unfermented, are extracted with boiling water in the quantities and in the manner directed on a previous page. The filtered decoction is carefully evaporated to a syrup. At this stage, constant stirring is begun, and kept up until the contents of the pan are quite dry. The temperature must be kept as low as possible to avoid burning the ink. In the meantime the ferrous sulphate and the gum are made perfectly dry, and are ground together to a fine powder. They are then mixed in the same way with the dry gall decoction. The brown mixture obtained is put at once into well-stoppered bottles, as it is very hygroscopic. A pinch of this powder immediately converts into ink the water in which it is stirred.

Logwood Chrome Ink Powder.

This is made by carefully evaporating the ink to dryness, or more simply by finely powdering very dry logwood extract and grinding it up with potassium chromate.

All ink powders should be put on the market and kept in bottles with ground-in stoppers, or in airtight packets, for although their quality is not deteriorated by the absorption of moisture from the air, they form lumps which are difficult to remove from the receptacles.

Cartons for Ink Powders.

The following process for making cartons or card boxes which will protect ink powder perfectly from damp can be confidently recommended : Heat paraffin wax to about the temperature of boiling water, and fill the box and its lid with it, and then pour it out at once. The sides of the box thus become perfectly airtight, so that it will keep ink powder quite dry, even in a damp room.

The chief points in the manufacture of ink powder are to keep the temperature of evaporation and drying so low that no burning can possibly happen, and to see that the ingredients are in a state of perfectly uniform mixture.

Frick's Ink Powder.

Gall powder	42	All well dried.
Ferrous sulphate	30	
Gum	15	
Alum	6	

The galls are ground up finely with the alum. The gum and the copperas are powdered separately, and then mixed with the rest. The powder is at once packed or bottled. The ink made by adding this powder to water gives a black sediment, from which it must be decanted. It is possible, however, to make an ink powder which is entirely soluble, by infusing the galls with water, evaporating the solution to dryness, and grinding up the residue with the other ingredients. The object of the alum in the recipe is to prevent moulding. If it is replaced by boric or salicylic acid, the acid chosen need only be about one-tenth per cent. of the powder.

Precision Ink Powder.

Gall extract	150
Ferrous sulphate	25
Copper sulphate	5
Alum	10
Gum	10

These ingredients, made absolutely dry and perfectly mixed together, give a powder which produces with water a very fine black ink of excellent quality.

G. Hell's Tannin Ink Powder.

Tannin	90
Copperas, powdered	90
Common salt	40
Potassium bisulphate	15
Sugar	40
Indigo carmine	5
Benzoic acid	3

The ink is made by dissolving 150 parts of this powder in 1000 parts of water.

G. Hell's Gall Copying Ink Powder.

Oxidised tannin (so-called)	1000
Sugar	60
Gum arabic	200
Copperas, powdered	250
Ferric sulphate	250
Carbolic acid	10
Phenol blue	50

For use as a copying ink the mixture is stirred up with five to six times the quantity of water. The so-called oxidised tannin is made by dissolving 500 parts of tannin and 50 parts of oxalic acid in a mixture of 400 parts of water, 50 parts of sulphuric acid, and 50 parts of glycerin, heating the mixture for three days on the water-bath, and then evaporating it to dryness.

Dieterich's Office Ink Powder.

Tannin	60
Ferric sulphate, dried	20
Potassium bisulphate	2
Sugar	10
Soluble aniline blue	5

For use the powder is boiled for fifteen to twenty minutes with 1250 parts of water.

Dieterich's Blue Ink Powder.

Resorcin blue M	6
Sugar	20
Oxalic acid	1

The mixture is dissolved in 1000 parts of water.

Dieterich's Red Ink Powder.

Eosine A	15
Sugar	30

Dissolved in 1000 parts of water.

Dieterich's Violet Ink Powder.

Methyl violet 3B	10
Sugar	10
Oxalic acid	2

Dissolved in 1000 parts of water.

Dieterich's Black Ink Powder.

Deep black E	20
Sugar	20
Potassium bisulphate	1

Dissolved in 1000 parts of water.

Logwood Ink Powder.

Logwood extract	500
Potassium chromate	1

Make the extract into a syrup with hot water, and stir in the chromate in concentrated solution in hot water. Evaporate to dryness with constant stirring, grind, and pack while still warm.

Ink Tablets.

Ink tablets are solid masses which dissolve in water, forming ink. The best inks for tablet-making are those in which the colouring matter is in solution. Chrome-logwood and horse-chestnut inks answer very well for the purpose. They are made by evaporating the ink to the right point, and then pouring it into tin trays with perpendicular sides about half an inch high. When the mass has set it is cut up with a sharp knife into square pieces, which are wrapped up in tin-foil. To gauge when the ink is sufficiently evaporated, let a drop of it fall on a cold iron. If it sets at once to a pasty mass, the ink is ready to be made into tablets. Special machines are also in use for moulding and stamping ink tablets. Ink tablets have the advantage that indigo carmine can be included in their composition, which, on account of the pasty nature of the indigo carmine, cannot well be done with ink powders.

Chrome Ink Tablets.

1.

Logwood extract	500
Potassium chromate	1
Alum	10
Gum	20

This gives a violet ink. Only as much water is used as is indispensable to obtain a perfect mixture.

2.

Logwood extract	100
Potassium chromate	1
Gum	10
Indigo carmine	20

This gives a beautiful ink. The writing changes from a blue to a deep black.

Horse-chestnut Ink Tablets.

Chestnut extract	100
Ferrous sulphate	10
Alum	2
Gum	5
Indigo carmine	5

The extract is made from the green husks of the horse-chestnut or from the young twigs, and evaporated down to the consistence of a paste.

XX.

PRESERVING INKS.

In former days the liability of every ink to mould was accepted with resignation as an unavoidable evil. The visible moulding of an ink is, however, only a symptom, and is attended by many undesirable changes. For example, an ink to which sugar has been added instead of gum to get a lustre often becomes so viscid that long threads hang from the nib, and it cannot be used for writing. This results from a peculiar form of fermentation of the sugar (the so-called viscous fermentation), and can usually be cured by shaking the ink with a freshly prepared gall decoction, and then allowing it to stand. In a short time a sticky black precipitate forms, and if the supernatant liquor is decanted it will be a useful black ink.

The fermentation processes which result in the formation of lactic acid have a much more serious effect upon ink, as they gradually destroy the colouring matter. If we find that the ink becomes pale and acquires a strongly acid taste, we may be sure that it will soon be useless. If the process is carried out in time, the ink can be saved by boiling it with some clean iron nails. The lactic organisms are thus killed, and the lactic acid is brought into combination.

When an ink becomes mouldy it gradually gets covered with a green matted layer of greyish-green fibres, which grow again as fast as they are removed, and with such speed that the whole surface will be covered again in a single night. Even if we throw away the ink and kill the germs adhering to the vessel by boiling it in water, the remedy is only temporary. When the vessel is refilled with fresh ink, it will soon get more germs from the air, and the growth will become as thick as ever. For a long time no means of combating the evil was known. It was certainly found that an excess of ferrous sulphate had a preservative action, but with the result of increasing the cost of manufacture, and causing the ink gradually to deposit a sediment and to produce characters which quickly turned brown. Additions of alum, too, have been found very effectual in preventing mouldiness, but cause the ink to corrode steel nibs, and, in the absence of considerable amounts of acid, precipitate the colouring matter in the form of an alumina-lake. This not only makes the ink pale, but makes it flow less freely, as may often be noticed in logwood inks containing alum.

It was long since noted that " alizarine " inks made with ordinary vinegar were very apt to become mouldy, whilst those made with pyroligneous acid rarely, if ever, went mouldy. The reason of this somewhat remarkable fact is that the pyroligneous acid contains a certain amount of carbolic acid, which is an extremely powerful disinfectant, and hence an efficient preventive of mould. It is better, however, to preserve ink by adding carbolic acid to it than by using pyroligneous acid in its manufacture. Carbolic acid is very cheap, and the ink is perfectly preserved by one-thousandth of its own volume, or even less. The acid possesses, however, a very penetrating odour, which is plainly perceptible even when the acid is highly diluted, and which, as the author has reason to know, has brought even very excellent inks into disfavour. Moreover, we have now in salicylic acid another excellent preservative which is odourless, and in small quantities is not poisonous ; it cannot be too strongly recommended to manufacturers of ink. According to the author's results, it will completely preserve from 5000 to 10,000 times its weight of ink. A little of it put into the ink-vat is an absolute safeguard against moulding. The salicylic acid can be added in the solid state, or dissolved in a little spirit.

Boric acid is another preservative not less to be recommended. It occurs in the form of glistening crystals, soluble in cold water with some difficulty, but easily soluble in hot water. This compound, too, will preserve 1000 times its weight of ink and upwards from mould. The best plan of using it is to hang it in a bag in the ink, so that it will gradually dissolve.

Many antiseptics, the often recommended corrosive sublimate for example, seem very ill-suited for preserving ink. Corrosive sublimate, in particular, is very poisonous as well as expensive, and we have in salicylic acid a completely innocuous and in every way suitable substance, which, for our purpose, is as powerful an antiseptic as the mercury salt.

Essential oils in general, and clove oil in particular, also possess antiseptic properties, and we therefore find the addition of a few cloves or a few drops of the oil to an ink recommended in many recipes. But an ink to which oil of cloves has been added necessarily acquires its smell, which is a disagreeable one to many persons. Besides, the preservative action of the clove oil is only limited. In time exposure of the ink to the air resinifies the oil, and it loses its antiseptic power completely.

Hence, from a general survey, the conclusion may be drawn that salicylic and boric acids are the antiseptics which offer the greatest advantages to the ink maker, and which should therefore be universally used.

XXI.

CHANGES IN INK AND THE RESTORATION OF FADED WRITING.

UNDER certain conditions iron-gall inks are extremely durable. In a place which is dry and free from mould spores the writing may remain a full black after the lapse of many centuries, as certain old documents amply prove. These two conditions are, however, very rarely combined. It is very difficult to exclude moisture completely, and even the best preserved writings betray the presence of spores under the microscope. These only demand the access of a little more moisture to develop and destroy the writing.

When a writing is destroyed by mould or damp, or by their joint action, the black colour gradually changes to brown, and finally to a pure rust colour. The ink is then entirely destroyed, and nothing remains but basic ferric sulphate. If the paper is then repeatedly wetted through the characters become paler and finally illegible.

When it is a question of restoring the legibility of a faded MS., the greatest care is needed, for unskilful treatment with chemicals may result in the absolute and irremediable destruction of the characters instead of their reproduction. One of the best means of deciphering illegible characters originally made with an iron ink is to convert the iron compounds still adhering to the paper into ferrous sulphide. As this is black, the characters at once reappear. This appearance is only temporary, however, as the sulphide is oxidised by the air, and the iron returns to the form of basic sulphate. The following modification of this process leaves the letters revived for at least a few days, so that, if necessary, the document may be copied. A cardboard box about 4 inches high, and of length and breadth corresponding to the sheets of paper containing the faded writing is used. The box has no lid, but can be closed by laying a sheet of glass on the top of it. Half-way up inside a frame is placed horizontally, and carries a netting of fine white silk or cotton threads. On the bottom of the box are placed two porcelain dishes containing yellow ammonium sulphide. The MS. is damped with a sponge and placed on the netting, and the box is covered with its glass lid. Care must be taken not to wet the paper too much, especially if the writing is on both sides, as then the letters are liable to soak through to the other side of the paper ; obviously, no rubbing is permissible.

The yellow ammonium sulphide may be bought, or may be prepared by dissolving sulphide of iron (FeS) in dilute sulphuric acid and passing the hydrogen sulphide gas evolved through a solution of ammonia until the solution turns yellow. It is then exposed to the light for a few days in a well-stoppered bottle until it turns dark yellow. In a short time after the MS. has been shut up in the box the letters turn brown, and the colour ultimately changes to black. As long as the MS. remains in the box the vapour of the ammonium sulphide will prevent any oxidation of the sulphide of iron, so that the MS. can be copied at leisure. It can also be removed from the box and photographed between glass plates.

In many cases the restoration can be made permanent by the following process :—

The MS. is dipped in a mixture of pure hydrochloric acid with 100 volumes of distilled water. The immersion must be momentary only, so as not to wet the paper below the surface. The hydrochloric acid used must be absolutely free from iron. The paper is then allowed to dry completely in the air, after which the writing is dusted over with finely powdered ferrocyanide of potassium from a pepper-caster, and then covered with a glass plate and slightly weighted. After a few hours the plate is removed, the paper dried, and the yellow powder is brushed off. If the paper had the proper amount of moisture when it was sprinkled, the characters will now be distinctly visible and of a blue colour, owing to the formation of Prussian blue by the action of the ferrocyanide on the iron of the ink which has been dissolved by the hydrochloric acid. The paper must now be freed from all traces of hydrochloric acid, which would in time efface the letters. To this end it is floated for twenty-four hours in a 2 per cent. solution of sodium carbonate crystals, and then rinsed in running water. The restored MS. must be kept in the dark as much as possible, or the light will cause the writing to fade again.

It is much more difficult to restore parchment than paper MSS., for the prepared skin contains substances which produce coloured compounds when subjected to the restorative processes. The process given by Moride consists in soaking the parchment in distilled water until it has swollen up, but all stirring or movement is carefully avoided. When thoroughly swollen, the parchment is drained, and dipped for five seconds in a 1 per cent. solution of oxalic acid in distilled water. It is then dipped into clean water, and, lastly, into a 1 per cent. solution of gallic acid. Here it remains until the writing comes out clearly. Finally, the parchment is rinsed with several lots of distilled water, and dried between folds of blotting-paper as quickly as possible.

The oxalic acid makes the iron salt still existing in the bleached ink soluble, so that it can again form black ink with the gallic acid. Unfortunately, the parchment itself often contains so much iron that the gallic acid makes it black all over, and in that case the writing cannot be deciphered. The same discoloration happens when the parchment is very mouldy, for the gallic acid then turns it brown. Hence it is important to restrict the quantities of chemicals used to the absolute minimum possible, and solutions are used still more dilute than those above given, and the process is repeated with them if necessary. In particular, the use of oxalic acid requires the greatest care, for if it acts too long, or is in too strong a solution, the writing, instead of being restored, will disappear for ever, as the iron of the original ink will pass from the paper into the solution. If it is a question of restoring valuable documents it is always advisable to experiment with a small portion first. We then find out how the whole will behave, and how far the use of reagents may be carried.

By exposing old parchments to the vapour of acetic acid, then letting them dry, and finally spreading them out on a glass and applying solution of gallic acid to the written surface, results at least equal to those achieved by the processes described above have been obtained. For this process, also, the parchment must first be swollen by soaking in water, or better, by exposure to steam, as long immersion often injures it.

Photographic methods of deciphering illegible documents are now used. These are based on the principle that by taking two negatives of the writing, one of greater intensity than the other, and superposing them, illegible characters are often made visible.

XXII.

COLOURED INKS.

ALTHOUGH among writing fluids black inks are the most important, as being those most largely used, there is also a demand from the public for inks of other colours. The origin of this demand is partly due to a desire to make distinctive appearances in different parts of a MS., and partly due to fashion and to individual preferences for coloured rather than for black inks.

In the present state of chemistry it is not difficult to prepare inks of any desired colour. Since the discovery of the coal-tar dyes we have been able to prepare coloured inks very easily by simply dissolving the appropriate dye. All possible colours can, however, be obtained in inks without coal-tar colours, and many of these inks are in great demand. No coloured ink, it may be observed, except perhaps real indigo carmine ink and some of the more recently discovered dyes, can compete with the black inks as far as durability is concerned. Writings made with most of them turn pale in a few months, and documents for long keeping should always be written with a good black ink. The requirements of coal-tar dyes for ink making are that they should yield relatively permanent writing, and be neither strongly acid nor strongly alkaline; obviously, they must also be soluble in water or in alcohol. Many dyes answering to these requirements are now manufactured, and the following may be mentioned as typical:—

Red Inks.—Eosine, erythrosine, phloxine, cyanosine, fuchsine, rubramine.

Orange Inks.—Acridine orange R, or mixtures of yellow and red dyes.

Green Inks.—Malachite green, iodine green, aniline green.

Blue Inks.—Methylene blue, patent blue, soluble blue, induline, paraphenylene blue.

Violet Inks.—Methyl violet, crystal violet, or mixtures of red and blue.

It should be noted that the different manufacturers of dyes do not always produce dyes with the same properties under a given name. Hence it is advisable always to obtain a particular dye from the same makers, and to make no change without preliminary experiments. With products of such intense tinctorial power differences in price are not of much importance. The natural colouring matters, such as Brazil wood, cochineal, saffron, etc., are still used, although only to a limited extent, in the manufacture of inks, but indigo is now almost entirely replaced by the synthetic product.

XXIII.

RED INKS.

In the preparation of red inks the various kinds of Brazil wood or redwood, cochineal, or an aniline dye are generally used. Both redwood and cochineal vary considerably in quality, and require much care in selection. The characteristics of both must therefore be known.

Redwood.

This is also called Brazil or Pernambuco wood. The tree (*Cæsalpinia echinata*) is indigenous to tropical America, especially to Brazil, which indeed owes its name to the appearance of the wood, *brasil* being the Portuguese word for glowing coals. The fresh wood is pink, but changes to a dark red on exposure to the air.

Several sorts are known in commerce. The best and richest in colouring matter is known as Pernambuco wood, after which come Sapan, Jamaica, Braziletto, and Bahama woods.

Redwood contains a colouring matter soluble in water, which gives very fine red lakes with alumina or tin. It is therefore much used by dyers and ink makers, although the colour is inferior to those obtainable with the much more expensive cochineal.

Cochineal.

This colouring matter consists of the dried bodies of an insect which feeds on various cacti, especially the nopal plant. Although indigenous to Mexico, both the insect and its food-plants have been acclimatised elsewhere, and nearly all tropical countries now produce large quantities of cochineal.

The dried insect appears in the form of silver-grey grains, the nature of which is easily recognised with a lens. The silver-grey sort is the best, when ground up to a brown powder. The black cochineal is inferior.

Great experience is necessary in buying cochineal, as it is so expensive that the most flagrant adulteration is often met with. A common occurrence is for cochineal from which most of the colouring matter has been exhausted to be resold as fresh material. Sometimes, too, the form of the insect is imitated with flour-paste, and the masses are coloured with a little cochineal and offered for sale.

A simple test of the quality of cochineal consists in grinding it up and treating the powder with a little caustic ammonia. If the cochineal is good, a very deep red solution of the dye will be produced immediately.

Before the aniline dyes were known, the finest red inks were those made from cochineal, but those made from anilines now dispute priority with them.

Redwood Inks.

Red Brazil Ink.

Pernambuco wood	280
Tin salt	10
Gum	20
Water	3500

The wood is boiled in the form of thin shavings with the water in a roomy vessel for about an hour. The decoction is then filtered. The tin salt is dissolved in a little water. If the solution should be turbid from the presence of basic salt, it is cleared by boiling it with a few drops of hydrochloric acid. The gum is now dissolved in the filtered redwood solution, and the tin solution is added. The ink is now finished, unless the colour of the writing done with it is too weak, in which case it must be concentrated by evaporation. The tin salt forms a red lake, which remains dissolved unless too much tin is added. If this is the case, some of the lake precipitates as a red flocculent deposit.

Pernambuco Ink.

Pernambuco wood	8
Alum	2
Gum	2
Water	60

Alumina forms a bright red lake with redwood, like tin salt. The wood is boiled with the water, and the gum and alum are dissolved in the filtered decoction. If this ink has a violet hue, which is likely to be the case, add powdered tartaric acid to it while it is boiling, putting it in a little at a time, until the desired pure red is produced. After each addition of tartaric acid boil for a few minutes, stir well, and try the colour by writing on paper.

Brazil Extract Ink.

Pernambuco extract	15
Alum	3
Tin salt	2
Tartaric acid	2
Water	120

Pernambuco wood extract comes on the market in solid masses like logwood extract. It gives a beautiful red solution in water, which answers as well for ink making as the decoction of the wood, and with the additional advantage of saving much time and trouble. Moreover, the solution can be made so strong that after-evaporation of the ink is unnecessary. Although very good, these redwood inks have been almost entirely superseded by cochineal or aniline inks, which are far superior to them in colour.

Cochineal or Carmine Inks.

Inks can be made direct from cochineal itself, and will be of great beauty and brilliance of colour, but for the very best inks the cochineal must first be converted into carmine. The labour of so doing is well repaid by the exceptional excellence of the resulting ink, and the trouble of making the carmine is compensated by the fact that the actual preparation of the ink from carmine is easier than from cochineal.

Preparation of Carmine.

Powder the best silver-grey cochineal as finely as possible, and boil it for three hours in water. Filter the hot solution quickly through a thick linen cloth. Boil the filtrate again, and add the substances needed to form the lake. Many such substances may be used, but only two can be thoroughly depended upon, and they should both be used together. These two are alum and tin salt, and if necessary, brilliance may be given to the colour by the cautious addition, drop by drop, of hydrochloric acid. The alum must be absolutely free from iron, or it will be impossible to get anything but a very unsatisfactory product. The best proportions are :—

Cochineal	20
Water	500
Alum	2
Tin salt	2

The alum and tin salt are added to the boiling solution, and the boiling is continued until everything is dissolved. The clear solution is then exposed in shallow dishes covered with sheets of glass for several weeks in a very bright sunny place. By this time the dark-red liquid will have lost nearly all its colour, and the carmine will have been deposited in the solid form, partly on the dish and partly on the surface of the liquid. It is separated by filtration, and carefully dried with blotting-paper. To get a fine and warm red it is absolutely indispensable that the dishes should get plenty of sun, so that the manufacture is impossible in any but the most favourable weather.

To get absolutely pure carmine, the product already described is dissolved in caustic ammonia. The solution is filtered, and the carmine is reprecipitated with acetic acid. The following is a recipe for a good carmine ink :—

Best Quality Carmine Ink.

Carmine	4
Caustic ammonia, dilute	500
Gum	10

Pour the ammonia on the carmine and gum, and heat on the water-bath nearly to boiling. Maintain the heat for ten minutes longer, and bottle the solution the moment it is cold, closing the bottles with good sound corks. If the ammonia is allowed to evaporate, the carmine will precipitate, as it is insoluble in water. The carmine can be re-dissolved, however, by adding a little ammonia and shaking.

The solution of carmine in ammonia is sold as soluble carmine, carmine solution, etc., and is much esteemed for water-colour painting.

It must be remembered that commercial caustic ammonia is not always of the same strength, and that an excess of ammonia makes the carmine solution purple or violet. Hence the ammonia should be added with care. If, in spite of every precaution, too much is put in, the right colour can be obtained by the very cautious addition of dilute hydrochloric or acetic acid.

Superfine Cochineal Ink.

Cochineal	40
Ammonium carbonate	2
Alum	2
Water	200

The ammonium carbonate is dissolved cold in the water, and the solution is poured on to a mixture of the alum and cochineal, both finely powdered, and the whole is shaken every quarter of an hour for three or four hours. By that time the extraction of the colouring matter of the cochineal will be complete, and nothing remains but to filter the ink.

The alum is required to precipitate from the ink other substances which are extracted from the cochineal together with the colouring matter, and which would otherwise decompose in the ink. When this happens, the ink turns thick and rapidly becomes mouldy, at the same time emitting such a disagreeable odour that many persons would throw the ink away long before it became unusable.

Indelible Silicate Carmine Ink.

This ink, invented by Böttger, is made by grinding up carmine with water-glass solution to a thick paste, to which more water-glass is then added till the ink has the desired colour and consistency. The ink must be kept in well-closed bottles, and only so much must be poured out as is required for immediate use. Exposure to the air makes the ink first gelatinise, then solidify to a glass. This ink is distinguished not only by its beautiful and permanent colour, but by being the most indelible of all red inks. When made of the proper degree of thinness it penetrates deeply into the paper, and can only be removed by caustic alkalies. Even these do not efface it completely.

Odourless Carmine Ink.

Cochineal	80
Crystallised sodium carbonate	160
Tartar	500
Alum	40
Gum	80
Water	1800
Spirit	100
or Salicylic acid	2

Dissolve the sodium carbonate in 1600 of the water, and soak the cochineal, finely powdered, in the solution for several days, with frequent stirring. The whole is then boiled, and the alum and the tartar are added in powder. This causes the liquid to froth very much, so that the boiling vessel must be roomy, and the powder must be put in a little at a time. After half an hour's boiling the liquid is filtered, and the remaining 200 of water poured boiling through the residue on the filter. The gum is then dissolved in the total filtrate. The alcohol or salicylic acid is used as a preservative, as the ink is very decomposable. Salicylic acid leaves the ink without smell and unalterable.

Patent Red Ink.

Cochineal	10
Tin salt	2
Sal ammoniac	2
Water	200

The colouring matter is fully extracted from the cochineal by boiling it in the water. While the liquid is still warm it is treated with ammonia and filtered. The filtrate is warmed and is mixed first with the sal ammoniac and then with the tin salt.

Cheap Cochineal Ink.

Pernambuco wood	60
Tartar	15
Alum	15
Gum	15
Water	500
Cochineal	5
Strong spirit	60

Boil the Pernambuco wood with the water for 1½ hours. Then add the tartar and the alum, and boil for another hour and a half. The gum is next added, and then the alcohol with which the cochineal has previously been exhausted by a week's digestion.

If the residual wood is treated with all the other ingredients again, but with one-fourth of the quantity prescribed for each in the above recipe, a fresh lot of ink will be obtained which can be mixed with the first.

Purple Ink.

Logwood extract	15
Crystallised verdigris	10
Alum	50
Gum	30
Water	800

The four solids are dissolved separately, and the four solutions are then mixed. Should the shade be too bluish, a few drops of very strong vinegar or of a carmine ink will correct it.

Carmine Purple Ink.

This is made by carefully adding solution of indigo carmine to a carmine ink, whereby the pure red of the latter may be changed to violet or purple as required.

Purple Carthamine Ink.

Safflower carmine	200
Gum	750
Cream of tartar	30
Sugar	75
Water	6000
Carbolic acid	5

Hell's Carmine Ink.

Carmine	20
Citric acid	10
Ammonia	250
Water	750
Gum arabic solution	30

The carmine and citric acid are treated with ammonia and left for some days, after which the mixture is diluted with the water and filtered, and the gum solution is added to the filtrate.

Red Magenta Ink.

Magenta, which is so largely used in dyeing, makes very beautiful red inks. It is sold in green crystals which form a dark red solution in spirit.

Magenta	2
Gum	5
Spirit	10
Water	100

The magenta is dissolved in the spirit, which must be as strong as possible, 90 per cent. at least, with the aid of gentle heat. In the meantime, the gum is dissolved in the water, and the solution is filtered and heated. As soon as it is boiling the magenta solution is poured into it in a thin stream, with constant stirring.

Eosine Ink.

Eosine is a splendid scarlet dye. Red inks made with it do not surpass the magenta inks in beauty, but have advantages in the brilliance of the written characters. They are made from the crystalline powder, of which commercial eosine consists, exactly in the same way as a magenta ink.

Dieterich's Eosine Ink.

Eosine A	15
Sugar	30
Distilled water	1000

Dieterich's Eosine Copying Ink.

This is made in the same way as the preceding ink, with the difference that 25 parts of eosine are used, and a suitable amount of glycerin or gum added.

XXIV.

BLUE INKS.

THE blue inks that deserve most attention are the solutions of water-soluble blue aniline dye and indigo carmine. They are the most deeply coloured, and penetrate so deeply into the paper that they are difficult to efface.

INDIGO-BLUE INK.

Indigo carmine	10
Gum	5
Water	50-100

Dissolve the gum in water and then the indigo carmine, and add more water until the writing is of the proper colour.

PRUSSIAN BLUE INKS.

Indigo-blue does not show so well on paper as Prussian blue. This, as sold, is insoluble, and although it can be used as such, does not give such good ink as the soluble Prussian blue. Soluble Prussian blue is also much used as a washing blue, and the ink maker should therefore make it for himself.

MANUFACTURE OF SOLUBLE PRUSSIAN BLUE.

Mix crude hydrochloric acid with one-tenth of its weight of nitric acid, and then add a weight of distilled water equal to that of the hydrochloric acid. Saturate the mixture with pieces of iron. As soon as it has dissolved as much of the metal as it can, which will take a few days, decant the solution of chloride of iron through a filter. In the meantime a weight of ferrocyanide of potassium equal to that of the hydrochloric acid has been dissolved in ten times its weight of distilled water, and is now gradually added to the iron solution until no more blue precipitate is formed. No notable excess of either ferrocyanide or chloride should be used. The precipitate is washed several times with water by decantation, and finally filtered off. The paste from the filter is ground up with one-tenth of its weight of crystals of oxalic acid, and water gradually added until a clear sky-blue solution is obtained, which can be used at once for ink-making.

The trouble of making the iron solution can be avoided by using bought ferrous sulphate, but that salt must first be converted into ferric sulphate by contact for a few days, in solution with one-tenth of its weight of nitric acid. The solution is then used as above directed for the solution of chloride of iron. In either case, the Prussian blue must not be allowed to dry before treatment with oxalic acid.

If the ink maker buys his Prussian blue he must buy the best, usually called Paris blue, and must prepare it for solution in oxalic acid in a way to be presently described. The bought Prussian blue, being dry, requires far more oxalic acid to dissolve it than it would do had it not been allowed to dry. The result is an ink costing much more to make, and, owing to the large excess of acid which it contains, attacking steel nibs vigorously. To prepare the purchased pigment for solution it is mixed with its own weight of concentrated sulphuric acid and left for twenty-four to thirty-six hours in it. The whole lot is then poured into a large excess of water, and the precipitate washed with water by decantation until the wash waters give no blue coloration with a solution of potassium ferrocyanide, and are therefore free from iron. The precipitate is then ground up while wet with oxalic acid as above described. Under these circumstances the oxalic acid will dissolve six times its own weight of Prussian blue, or eighteen times as much as it will dissolve of the dry commercial pigment.

Blue Post Ink.

Dissolve 17 of potassium ferrocyanide in 54 of water, and 17 of ferrous sulphate in 1540 of water. Mix and treat the blue precipitate with a mixture of—

Nitric acid	10
Hydrochloric acid	5
Water	500

After twenty-four hours pour off the liquid, and grind up the precipitate with 3½ of oxalic acid. Then add 4000 of water containing 160 of white gum in solution.

Blue Aniline Ink.

Dissolve water-soluble blue in water so that the writing is a good blue without metallic lustre, and thicken with gum. If a copying ink is wanted, add glycerin as well.

Dieterich's Blue Writing Ink.

Resorcin blue	5
Distilled water	970
Sugar	20
Oxalic acid	1

F. Schmidt's Aniline Blue Ink.

Aniline blue	10
Alcohol	40
Gum arabic	20
Water	500

The dye is dissolved in the alcohol and the gum in the water; and the two solutions are mixed.

Pakely's Dry Copying Ink.

Aniline blue	30
Alum	15
Water	2000
Glycerin	1000

This ink gives good copies without the need of moistening the leaves of the copying book.

XXV.

VIOLET INKS.

VIOLET inks have already been described in previous sections of this book, but there are other methods of making them. One way is to mix a red ink with a blue one, and in any case aniline dyes give inks of a much better colour than the violet inks already mentioned. The latter, however, have the advantage of being very cheap.

VIOLET ANILINE INK.

This is prepared by dissolving methyl violet in spirit. The alcoholic solution need not be boiled for the necessary dilution with water as is the case with magenta, but the water must nevertheless be added with care. The moment any precipitate begins to appear the addition of water must be stopped, and the liquid made clear again with a little spirit. The necessary amount of gum is then dissolved in the liquid.

DIETERICH'S VIOLET WRITING INKS.

Methyl violet	10
Sugar	10
Oxalic acid	2
Water	980

The methyl violet is treated with a little water, and, after standing for some time, is diluted with the remainder of the water and boiled with the oxalic acid and the sugar until the dye is dissolved.

Methyl violet	6
Acetic acid (30 per cent.)	5
Sugar	20
Water	980
Patchouli oil	1 drop.

This is made in the same way as the first ink.

Methyl violet	20
Distilled water	940
Sugar	10
Lactic acid	10
Oxalic acid	2

The violet aniline inks, although very beautiful, are not particularly durable, and can be easily and completely effaced by chemicals. The following recipe gives a more permanent ink :—

Violet Indigo Ink.

Make a solution of indigo carmine strong enough to be used as a blue ink, and add to it the proper amount of gum. Then add gradually a very thick solution of carmine, so that the ink passes through purple to violet. The ink should be tested from time to time during the making by writing with it. A still finer but less durable ink is made in the same way from a solution of Prussian blue and carmine.

Violet Copying Ink.

1.

Glycerin	10
Oxalic acid	5
Logwood extract	40
Alum	30
Water	800

2.

Potassium dichromate	5
Dissolved in water	100

Make solutions 1 and 2 separately, and then mix them. Boil the whole in a copper pan, add 50 of pyroligneous acid, and bottle.

XXVI.

YELLOW AND BROWN INKS.

A FULL yellow ink can be made in several ways, the simplest of which is to dissolve picric acid in hot water. Picric acid is sold in yellow crystals, which are very bitter and poisonous.

Picric Acid Ink.

Picric acid	10
Gum	2
Water	100

Boil all together. The water must be distilled water.

Dieterich's Writing Ink.

Aniline orange	15
Sugar	30
Water	1000

F. Schmidt's Brown Ink.

Aniline brown	15
Alcohol	40
Gum arabic	20
Water	500

The dye is dissolved in the alcohol, and the gum in the water, and the two solutions are mixed.

Yellow Gamboge Ink.

Gamboge is a resin which can be emulsified with water, although it will not dissolve. Heat 10 parts of gamboge in fine powder with 10 of spirit, and then mix it with 5 parts of gum arabic first made to a very strong mucilage with water. Then mix with 30 parts of water.

Imperial Yellow Ink.

Persian berries	280
Alum	28
Gum	36
Water	1000

Boil the crushed berries with the water for an hour. Then add the alum and boil for another hour. Filter and dissolve the gum in the hot filtrate.

Saffron Ink.

Saffron	10
Alum	10
Gum arabic	20

These constituents are mixed with a little water and left for a few days, with frequent stirring, and the liquid then expressed and diluted for use.

XXVII.

GREEN INKS.

GREEN, like violet, is a mixture, in this case of blue and yellow. Hence, by mixing a blue and a yellow ink in different proportions, every imaginable shade of green can be obtained. The best mixtures are picric acid with either indigo carmine or solution of Prussian blue. The following, however, are some recipes for some green inks which are not mixtures of blue and yellow inks :—

KLAPROTH'S GREEN INK.

Crystallised verdigris	4
Tartar	2
Water	16

The three ingredients are boiled together, filtered, and bottled.

GREEN CHROME INK.

Potassium dichromate may be used as the basis of a green which is not only of a bright green colour, but is also very durable.

Potassium dichromate	10
Hydrochloric acid	10
Spirit	10
Gum	10
Water	30

Mix the dichromate, finely powdered, with the acid, and let it stand for an hour, after which the spirit is slowly poured, with constant stirring, into the red solution thus obtained. The reaction is very vigorous, and the liquid froths and gets very hot, and gradually turns to a dark green. If the action gets too violent, a little cold water is added. To avoid boiling over, it is best to add the spirit in portions, waiting till the frothing after each addition is over before adding the next. The next step is to add sodium carbonate till all effervescence has ceased and a greenish precipitate just begins to form. The liquid is then left covered up for a week, filtered from the salts which have crystallised out, and diluted to the desired colour. Finally, the gum is dissolved. This ink penetrates the paper deeply, and gives green writing which is absolutely permanent and is very difficult to efface.

Stein's Green Ink.

1.

Indigo carmine	120
Gum	200
Water	3000

2.

Picric acid	15
Boiling water	720

Make solutions 1 and 2 separately, and then mix them.

F. Schmidt's Green Writing Ink.

Aniline green	12
Alcohol	42
Gum arabic	20
Hot water	500

The dye is dissolved in the alcohol, and the gum in the water, and the two solutions are mixed.

Dieterich's Green Ink.

Water-soluble methylene green	10
Distilled water	30

The dye is digested with the water for several hours and then added to—

Hot water	950
Sugar	20
Patchouli oil	1 drop.

XXVIII.

BLACK INKS FROM ANILINE DYES.

THE dyes principally used for the preparation of black inks from aniline dyes are induline and water-soluble nigrosine, or mixtures of the two.

DIETERICH'S BLACK INK.

Aniline green D	24
Ponceau RR	20
Phenol blue	1

This mixture gives a deep black ink when dissolved in water.

COUPIER AND COLLINS'S INDULINE INK.

Induline	20
Water	1000

DIETERICH'S WRITING INK.

Aniline green D	3	digested with 60 of cold water.
Ponceau RR	3	
Phenol 3F	3	
Hot water	900	
Sugar	20	
Carbolic acid	1	

VILLON'S COPYING INK.

Nigrosine	60
Dextrin	80
Glycerin	80
Water	100

XXIX.

METALLIC INKS.

In ornamental writing it is customary to use inks that produce characters with a metallic colour and lustre. Such inks can be made in two ways. One can either use the metals themselves or certain dyes which, under particular circumstances, acquire a metallic lustre. If an unalterable metallic ink is wanted, it must be made from a precious metal, gold or silver, for all other metals oxidise in time and change their colour. This is particularly true of copper.

Real Gold and Silver Inks.

To produce these the metal, in the form of leaf, is ground up with gum and water in a mortar till even a strong lens shows no sign of metallic lustre. Water is then added, but the ink must be left thick or the metal would rapidly settle to the bottom. Even then, the ink must always be well shaken every time it is used. In the case of gold it is better to dilute it with a solution of picric acid than with water. Then much more water can be added, and the writing will nevertheless have a fine gold colour and lustre. This use of picric acid lessens, too, the extreme costliness of the ink.

Copper Ink and Bronze Ink.

These are made in the same way, but with the use of the proper foil. In time the writing becomes dull, and in damp places turns green.

Imitation Gold Ink.

This is made from *aurum musivum*, which is ground up with a gamboge ink. This ink, although not so beautiful as the real gold ink, has the advantage over bronze ink that it keeps its colour.

Lead iodide, which forms glistening golden spangles, can also be used for imitation gold inks. Equal quantities of potassium iodide and lead acetate are mixed, and treated on a filter with twenty times their weight of boiling distilled water. The lead iodide, which separates from the filtrate, is then ground up with a solution of gum.

Imitation Silver Ink.

For this ink tinfoil is ground up with the gum, but a better imitation can be made with aluminium foil or leaf. The aluminium keeps its silver colour permanently.

Coloured Inks with a Metallic Lustre.

It is possible to produce inks with any desired colour with a metallic colour by the use of coal-tar dyes. The solution of the dye is thickened with gum, and ground up with real or imitation silver, when an ink having a metallic lustre and the colour of the dye used is obtained. For yellow, red, and brown, gold or a golden yellow alloy is used; also a very concentrated alcoholic solution of magenta. The writing is a dark red, and in certain lights shows the green and gold lustre of the crystallised magenta, In addition to the inks described in the preceding pages, there are other liquids which are applied to special purposes, such as artists' ink or Indian ink, used for making permanent drawings, lithographic inks, marking inks, and, lastly, sympathetic inks, which are the inks that disappear, or become visible, or change their colour under special treatment. While the sympathetic inks must be reckoned more or less as toys, the remaining kinds just named are widely used, and their manufacture is remunerative.

XXX.

INDIAN INK.

THE Chinese, Japanese, and other Asiatic races write with a brush with a solid ink rubbed up with water like a pigment. This Chinese or Indian ink is remarkable for the durability and lustre of its colour. These properties have caused it to be extensively used by architects and engineers, and in general by people who have to make permanent drawings.

Chinese ink is one of those products which, notwithstanding the advance in chemical knowledge, has not been completely imitated, and the imported product always receives the preference over that made in Europe. Most European-made Indian inks are distinctly brown when diluted to any great extent, and lack the lustre of the true Asiatic product.

We do not know exactly what method of manufacture is still adopted in China. There are reports, which, however, require confirmation, that the process consists in burning certain plants in a limited supply of air, and passing the smoke through very long paper tubes. The soot deposited in those parts of the tubes which are furthest from the fire, i.e. the finest particles, is selected for making the ink. Other accounts say that the smoke used is obtained principally by burning sesame oil. This is burnt in lamps in such a way that it gives a very smoky flame. It appears not impossible that a product which is manufactured over such an extensive area may be made from various raw materials and in various ways.

When genuine Indian ink is examined it will be found that it consists mainly of carbon in a state of excessively fine subdivision, with a binding material probably consisting of gum, but also containing camphor (up to 2 per cent.) and musk. The special smell of real Indian ink is certainly due to the presence of musk, of which only very minute quantities are needed to produce it.

Two distinguishing features of genuine Indian ink are that the carbon is pure, i.e. free from tarry matter, and is in a state of extraordinarily fine subdivision. A process has now been devised by which such carbon can be prepared without much difficulty. A fuel rich in carbon, such as petroleum or purified oil of turpentine, is burned in lamps with a feeble supply of air. The smoke is passed through a zinc tube at least 100 feet long, and with a slight upward inclination from the lamp, so as to produce the necessary weak draught. The lampblack which accumulates in the parts of the tube near the lamps can be used with advantage for articles less expensive than Indian ink. It makes excellent printers' ink, for example. That which is gathered from the most remote part of the tube is quite fit for the finest Indian ink, after it has been purified from the traces of tarry matter which adhere to it, and which impart the brown colour to inferior inks. This purification is effected by making the lampblack into a thick paste with nitric acid by means of a glass or porcelain spatula. The mass is then brought to the consistence of honey by adding a little distilled water, after which it is heated in a porcelain basin until dense fumes of nitric acid are evolved. In this way a large part of the tarry matter is completely destroyed, and, moreover, it produces finely divided carbon by its destruction. The mass is now largely diluted with water, and allowed to settle. The dilute acid is then poured off, and the washing with water is once repeated. The sediment is next boiled for half an hour with a strong solution of caustic soda. This destroys the rest of the tarry matter, and the carbon left, after repeated washing with water, is in a state of the finest possible subdivision and practically chemically pure. It is then dried in vessels covered to keep out dust, and made into a paste with a clear solution of gum. This paste is thickened by stirring and heating until it sets quite hard on cooling. Just after it has been removed from the source of heat a little tincture of musk is stirred into it. The mass must then be cooled slowly in a warm place. When it begins to crack it is kneaded into a lump which is rolled out into a flat plate and dried further until it can be cut into the usual quadrangular sticks, and will take a clean impression of a stamp. The sticks are formed in metal moulds, having characters and designs on the inside, and it is to be feared that sometimes these designs have the object of representing the product to be of Chinese origin. The overflow from the moulds is cut off with a sharp knife, and the rods are ejected by inverting the mould and tapping it. Then they are perfectly dried, and, if wished, wrapped partly or entirely in gold or silver leaf. If any cracks appear in them, these are filled with fresh paste and smoothed over. The pieces must be hard, have a lustrous pure black surface, and show a perfectly uniform and compact fracture.

Indian ink prepared as above directed and in which care has been bestowed on the moulding as well as on the manufacture can hardly be distinguished from the Asiatic-made article, even by experts. In uniformity, colour, and lustre it is equal to some products of Chinese manufacture, and even surpasses some genuine Indian inks.

A somewhat inferior article can be made from ordinary soot by boiling it with caustic soda lye, washing, and mixing it with gum as above directed, and then moulding the paste in the usual way.

XXXI.

LITHOGRAPHIC INKS AND PENCILS.

LITHOGRAPHERS require special inks or pencils, according to the particular method of procedure. If the stone is polished the drawing is executed in lithographic ink on it with a pen or brush. When the stone is then treated with a dilute acid the ink protects the parts it covers, which therefore become raised above the etched part of the stone, and the sheets can then be printed from it. When, however, MS. is to be reproduced by lithography, the MS. is written on prepared paper with lithographic copying ink. The paper is then laid, writing downwards, on the smooth stone, and the ink is transferred to the stone by pressure. The acid is then used as before.

When the lithography is required to reproduce the effect of a chalk drawing special pencils are used, by means of which the design can be drawn on the roughened (granular) surface of the stone. These pencils are essentially solid inks which can impart their pigment to the stone.

The inks and pencils used for lithography must always contain acid-resisting substances, and must also be capable of receiving a film of printing ink. Such substances are fat, rosin, and wax when converted into a soap.

Lithographic Ink.

Water	140
Gum lac	100
Mastic	30
Rosin	10
Tallow soap	70
Soot	32

For making this ink composition a copper boiler with a lid and a copper pan with a spout are required. All the ingredients, except the wax, are first melted together in the pan, and uniform admixture is effected by thorough stirring. The wax is heated by itself in the larger vessel until it can be ignited, and after its ignition the contents of the pan are stirred into the burning wax. As soon as all the ingredients are in the boiler, the flame of the wax is extinguished by putting on the lid, and the heat is moderated until the mass only keeps in fusion. It is then ladled out into metal moulds which give it the same shape as the rods of Indian ink.

For use, this ink has to be ground up with warm water, just like Indian ink. Any ink thus mixed which is to be left overnight should be covered up to keep it moist, for if it has to be rubbed up again it will very likely form lumps which will spoil the work, more particularly if a brush is used.

It has been recommended to dissolve the ink in hot water and bottle it. Although this saves the constant grinding up, the practice is not good, as it does not yield such a uniform and reliable ink.

French Lithographic Ink.

Shellac	30
Mastic	6
Potassium carbonate	6
Hard tallow soap	6
Lampblack	2

Melt the soap with the shellac and the mastic, and stir the carbonate and the lampblack into the melted mass. As soon as the mixture is uniform it is cast in the moulds.

Vienna Lithographic Ink.

Wax	18
Soap	18
Shellac	14
Rosin	6
Tallow	10
India-rubber	2
Oil of turpentine	5
Lampblack	6

Melt the first five ingredients together, and heat until the mass begins to bubble. Then stir in the lampblack and also the india-rubber, previously dissolved in the turpentine. When the smell of the turpentine has nearly disappeared, cast the mass into sticks.

Munich Lithographic Ink.

Wax	20
Tallow	10
Shellac	20
Soap	20
Sodium carbonate	30
Lampblack	10

Melt all the ingredients together at a strong heat, and stir thoroughly.

English Lithographic Ink.

Virgin wax	12
Tallow	12
Hard tallow soap	12
Shellac	24
Mastic	16
Venice turpentine	2
Lampblack	22

Heat the turpentine, and add to it the shellac, the mastic (both finely powdered), the tallow, the wax, and the soap in the order named. Finally mix in the lampblack intimately. The tough mass produced on cooling is rolled out and cut into sticks or cast in moulds.

VIETTE'S LITHOGRAPHIC INKS.

A.

(For Writing on Stone.)

Gutta-percha or india-rubber	1
Dissolved in—	
Oil of turpentine	7
Tallow or wax	2
Lampblack	3

B.

(For Reliefs to be Etched on Stone.)

Gutta-percha or india-rubber	2
Oil of turpentine	7
Tallow or wax	2
Bitumen	1
Lampblack	3

C.

(For Etching in Relief on Metals.)

Gutta-percha or india-rubber	3
Oil of turpentine	7
Tallow or wax	1
Bitumen	1
Colourless varnish	1
Lampblack	4

The solution or suspension of the rubber or gutta-percha in the oil of turpentine is facilitated by heating them beforehand in a flame.

Lithographic Chalk.

This is used for drawing on the stone. It must be compact enough to take a sharp point without breaking, like a good lead pencil, and give a uniform stroke with a light pressure.

London Lithographic Chalk.

Wax	30
Tallow	25
Soap	20
Shellac	15
Lampblack	6

Melt all these ingredients together, and heat till the mass can be ignited. It is then allowed to burn for a time, which requires some experience to judge. The condition of the mass can, however, be ascertained at any time by extinguishing it by putting the cover on the boiler, and then making a stick of the mixture and trying how it will write. If the stick will not bear a sharp point, having some elasticity and producing a uniform black line, the mass in the boiler must be ignited again, and tested once more a few minutes later. The finished mass is rolled out on a hard surface, and made into pencils the thickness of a goose quill and about 3 inches long.

French Lithographic Ink.

Tallow	100
Soap	85
Shellac	70
Mastic	10
Lampblack	10

Melt these ingredients together and ignite, and proceed as directed in the last recipe.

Engelmann's Lithographic Chalks.

Soft Chalk.

Yellow wax	32
Dry white soap	24
Tallow	4
Dilute nitric acid (1 : 7)	7
Lampblack	7

Hard Chalk.

Yellow wax	12
Soap	8
Shellac	10
Sodium carbonate solution	1
Tallow	2
Lampblack	4

Transfer Inks.

These inks, also termed autographic inks, are intended for transferring a writing or drawing to the stone, which can then be printed from directly it has been etched. This affords a means of securing a number of copies, which is very important for circulars, letters, plans, etc.

There are, however, certain difficulties in the preparation of these inks, for it is necessary to have a liquid which, besides possessing the properties of an ordinary ink, will cling fast to the stone and give copies for a considerable time. For common work, such as a circular, the paper used may be any usual paper, provided it is not too rough; but if fine work is necessary, as in making copies of a pen-and-ink drawing or of an architect's plan, satisfactory results can only be obtained with prepared paper.

Preparation of the Paper.

By following strictly the following recipe the finest line or point can be faultlessly reproduced in the copies. The stone can be etched immediately the transfer has been made, and many thousands of good copies can be printed off.

A fine, strong, unsized printing paper is spread out on a smooth board, and over it is poured a 10 per cent. solution of gelatin. The board is then tilted and the gelatin run off, and a 5 per cent. solution of tannin is next poured on. The paper is again drained and dried. The two processes and the drying are then repeated a second or a third time, and the paper is finally calendered. This paper will not only transfer, as above stated, the finest lines of a drawing, but will also take the minutest details of a copper or steel plate, and transfer them to the stone.

Fritz's Transfer Compositions.

A.

(For Transparent Paper.)

Finest gelatin	4
Colourless glycerin	4
Alcohol, 36 per cent.	1
Water	40

The composition must be applied in a very thin layer and uniformly distributed.

B.

(For Opaque Paper.)

Finest wheat starch	5
Dextrin	1
Glue	2
Finest precipitated chalk	1

As a distinguishing mark a little gamboge may be applied to the paper, lukewarm, with a sponge and brush.

When the drawing or writing has been laid on the stone the two must be forcibly pressed together in a press several times. The paper is then carefully taken off. The repetition of the pressure is made necessary by the fact that the stone takes an appreciable time to retain the ink so firmly that it will not be affected by the etching with dilute nitric acid.

Best Autographic Ink.

Wax	110
Tallow	30
Soap	110
Shellac	50
Mastic	40
Rosin	10
Lampblack	30

These are melted together in an iron vessel, and the temperature is then raised until disagreeable vapours are largely produced. The mass is then cast into moulds or rolled into cylinders.

The autographic inks can also be used very well for ordinary writings with a steel pen, so long as the letters are not too small.

Autographic Drawing Copying Ink.

Ground Mass.

Wax	70
Tallow	75
Soap	60
Copal	45
Shellac	70
Mastic	70
Pitch	10
Linseed oil	10
Sulphur powder	10

The copal is first fused with the linseed oil, and so strongly heated that thick, strong-smelling fumes appear. The soap is then added, then the tallow, then the wax, and lastly the other resins. The whole is next strongly heated and ignited. During the combustion the sulphur is sprinkled on to the mass, which is continually stirred. The combustion must be continued until about three-quarters of the mass has been burnt away. The fire is then put out by covering the vessel with its lid.

Autographic Ink, No. 1.

Ground mass	12
Distilled water	100
Indigo carmine	5

The ground mass is boiled with the water until the liquid is reduced to half its volume. The clear brown liquid is then poured off, and the indigo carmine dissolved in it.

If the ground mass has not burned long enough the ink will not give good copies, as it will dry too quickly. If, on the other hand, the combustion has been unduly prolonged, the ink will not adhere properly to the stone. It should also be noted that when the writing is transferred to the stone the back of the paper should be well damped, to facilitate the transfer of the ink.

Autographic Ink, No. 2.

Wax	200
Soap	60
Tallow	32
Shellac	16
Black pitch	8
Lampblack	46

The ingredients are melted together and stirred to a uniform mixture, which is gradually heated until it fumes of water, or with a solution of 10 oz. of iron ammonium citrate and 10 oz. of potassium ferricyanide in 60 oz. of water. The paper is then dried and exposed to the sun for an hour under the copy, after which the paper is developed with a 10 per cent. solution of ferrocyanide of potassium, thoroughly rinsed and dried. The writing, etc., will then appear white on a blue ground.

Copying Process for Indian Ink Drawings and Engravings on Copper or Wood.

Dissolve oxalic acid in cold water, heat the solution to boiling-point, and add as much molybdic acid as the boiling solution will dissolve. The solution is kept in bottles of black glass. Paper is soaked with this, and dried in the dark-room, and then exposed under the photograph, drawing, or engraving in an ordinary printing-frame. The copy is thus obtained white on a dark blue ground. If the paper of the engraving, etc., is very thick, the passage of light through it must be facilitated by lightly rubbing it on the back with petroleum.

XXXII.

INDELIBLE AND OTHER INK PENCILS.

Indelible Ink Pencils.

It is unnecessary to enlarge on the usefulness of these articles, which combine the convenience in use of a lead pencil with the production of ink-writing with its special appearance and durability. The manufacture of ink pencils has received a great impulse from the discovery of the coal-tar colours, but although many makers put them on the market, certain faults have restricted their use within somewhat narrow limits. Some are too soft, so that they absorb water from the air and make smudgy writing; others so hard and brittle that they break whenever any attempt is made to sharpen them.

The prime conditions of making a really usable ink pencil are to have the ingredients in a state of the finest possible subdivision, and to bring them into sufficiently compact rods by high pressure. The characters then come out strongly, with gentle pressure on the point of the pencil if the paper is slightly damp. The aniline dyes used include magenta for red, water-soluble blue and methyl-violet for their respective colours, and nigrosine for black.

Faber's Ink Pencils.

	Aniline Dye.	Graphite.	Kaolin.
1.	100	75	25
2.	46	34	24
3.	30	30	40
4.	25	24	50

The three ingredients are thoroughly mixed, and the mixture is then forced through holes in a plate, so as to form it into rods, which are finally dried. No. 1 is very soft, No. 4 very hard.

Pencils of this type are known both as "indelible ink pencils" and "copying ink pencils," although they are seldom, if ever, used for copying purposes.

According to another recipe, 10 lb. of best logwood are boiled with 100 lb. of water. The decoction is evaporated down to 100 lb., and a solution of chromium nitrate is added till the precipitate at first formed has redissolved to a bluish-black liquid. This is evaporated on the water-bath till it can be formed into rods, after being mixed with three to four times its weight of special clay and solution of gum-tragacanth. This recipe seems to the author faulty, and gives results very inferior to those obtained with the aniline dyes.

PENCILS FOR WRITING ON GLASS, PORCELAIN, AND METAL.

The ingredients are thoroughly mixed, and shaped into sticks by hydraulic pressure. The sticks are then encased in wood like pencil-leads. Their use requires a fair amount of pressure, but the writing cannot be washed away with water.

1. *Black.*

Lampblack	10
Wax	40
Tallow	10

2. *White.*

Chalk	40
Wax	20
Tallow	10

3. *Pale Blue.*

Prussian blue	10
Wax	20
Tallow	10

4. *Dark Blue.*

Prussian blue	15
Gum	5
Tallow	10

5. *Red.*

Cinnabar	20
Wax	60
Tallow	20

6. *Yellow.*

Chrome yellow	10
Wax	20
Tallow	10

Pencils for Writing on Glass.

1.

Water	16
Red lead	8
Tallow	2-4

The ingredients are thoroughly mixed, melted together, and cast into sticks. The variation in the amount of tallow enables the pencils to be made harder or softer.

2.

Tallow	5
Wax	10
Tallow soap	10
Red lead	10

The red lead is stirred in after the other three ingredients have been melted together. The mass is shaped into cylinders before it is quite cold, after having been stirred to the last possible moment. The sticks tend to become brittle with age, and should therefore be kept in a warm place.

XXXIII.

MARKING INKS.

THESE are the inks used for writing on textile fabrics. It goes without saying that they must resist washing, and must be unaffected by immersion in water for weeks on end without change. They have, however, to resist also the various substances used in laundries. It is often required of them in addition that they should be still distinctly visible when the place marked has been dyed and then bleached again.

Only a few substances are known which answer fully all the requirements made in respect of a marking ink, and only those which depend for their colouring matter on free carbon are absolutely indelible.

Solutions of the precious metals, gold, silver, platinum, and iridium (a rare metal closely allied to platinum), have the property of being decomposed by organic matter, the metal being separated out in an extremely finely divided state, and forming a very distinct writing.

Silver compounds are decomposed by light alone, and turn black by the separation of very finely divided metallic silver or of a silver oxide. This circumstance, as well as the fact that silver is the cheapest of the precious metals, makes silver the most suitable for metal marking ink. There are, however, organic dyes which can be brought into a form in which they are soaked up by a fabric, and form with it insoluble compounds. Such a substance, for example, is indigo-white, which is almost entirely indelible on animal fabrics such as wool and silk. The organic marking inks have here a great advantage over those prepared from metals, for writings made with any metallic salt can be eradicated without leaving any trace and with comparative ease. Silver can be removed by solution of cyanide of potassium, and gold and platinum by chlorine water. Writings done with indigo-white and carbon, on the other hand, are practically indestructible, for even after the indigo has been removed the carbon adheres to the fibres with such tenacity that it cannot be removed without radically injuring the fabric.

Metallic Marking Inks.

A.—Silver Inks.

There are numerous recipes for marking inks of which the basis is silver. In all cases, without exception, the salt of silver used as the primary substance is the nitrate. On account of the price of this salt, those who use it in anything like large quantities should make it for themselves, especially as this can be done very easily.

Preparation of Silver Nitrate.

The first condition of suitability for marking inks of nitrate of silver is freedom from copper, and a perfectly pure salt can be obtained as follows :—

Pour nitric acid over some silver in a glass vessel. The metal dissolves rapidly with evolution of suffocating fumes of nitrous oxides. The solution obtained will be more or less blue, according to the amount of copper present. It is diluted with distilled water and treated with hydrochloric acid. The white, curdy precipitate settles quickly, and when the further addition of hydrochloric acid produces no more of it the supernatant liquid is decanted through a filter, on to which the precipitate is received. Here it is washed with distilled water until the filtrate gives no blue colour with ammonia, a sign that all the copper has been washed away.

The precipitate is then put, together with strips of zinc, into somewhat dilute hydrochloric acid. The colour of the chloride of silver soon changes to a peculiar metallic grey as it becomes reduced to the metallic state. After some days the mass is filtered off, and the pure silver on the filter is washed with distilled water until a sample of the filtrate remains perfectly clear on the addition of ammonia. The silver is then dissolved in nitric acid, which must be free from hydrochloric acid, or some of the silver will return to the state of chloride and remain undissolved. The solution is next evaporated, but is not allowed to boil for fear of loss by spirting. As soon as the contents of the dish are solid the heat is raised until the salt fuses, and is then immediately removed. The nitrate of silver is then obtained in the form of a colourless crystalline mass. It gradually blackens when exposed to the light, and should be kept in the dark or in orange-coloured bottles. It should leave no residue on solution in water.

A simpler method of preparation is to dissolve the impure silver-containing copper in pure nitric acid, evaporate the solution, and heat the residue. This then turns dark and evolves fumes of nitrous oxides, for the nitrate of copper decomposes at a lower temperature than the nitrate of silver into nitrous compounds and black oxide of copper. The secret of success in this method, therefore, is to work at such a temperature that the nitrate of copper is decomposed, but not the nitrate of silver. The process is regulated by occasionally taking a sample of the fused mass on the sharp point of a glass rod. This sample is dissolved in water and tested with ammonia. As soon as this ceases to produce a blue colour the decomposition of the copper salt is complete, and the mass is at once allowed to cool. The grey solid thus obtained consists of nitrate of silver mixed with finely divided cupric oxide, which is removed by dissolving the nitrate of silver in distilled water and filtering off the solution for use.

Whichever of these two methods of preparing silver nitrate is adopted, it is necessary to fuse the salt obtained to get rid of the last traces of the nitric acid, which would otherwise damage the fabric by passing into the marking ink.

Preparation of the Fabric for Marking.

It is, of course, possible to write with a mere solution of nitrate of silver, but the writing will then run, and will, besides, not adhere strongly to the fibre. But if the fabric, whether linen, cotton, silk, or wool, is first prepared at the spot to be marked, we can use the plain nitrate of silver as a marking ink, either with the pen or with a rubber stamp, and get perfectly sharp letters. For this purpose equal weights of sodium carbonate crystals and gum arabic are dissolved in a weight of water equal to ten times the weight of either, and the solution filtered. The place to be marked is soaked with this solution and dried, and when quite dry smoothed with a hot iron. The solution of nitrate of silver, being colourless, must be coloured with some inactive colouring matter to make the writing visible from the first.

Silver Marking Ink.

Nitrate of silver	4
Water	40
Gum	4
Lampblack	2

Dissolve the gum by itself in half the water, and mix the solution carefully with the lampblack by grinding. Then dissolve the silver salt in the rest of the water, and mix the two lots by thorough shaking. Other indifferent colouring matters may be substituted for the lampblack, e.g. finely powdered indigo or a solution of sap green, or of any soluble aniline dye, such as water-soluble blue, only enough being taken in each case to make the writing legible from the first.

When the marking is done it is left exposed to the light, if possible to the direct rays of the sun, when the writing blackens by the formation of metallic silver or of a silver suboxide. The nitric acid which is set free at the same time is neutralised by the sodium carbonate used in preparing the fabric. If this preparation has been omitted, delicate fabrics would be worn into holes by the acid. As soon as the writing ceases to darken, the marked place is rinsed in warm, soft water. After that the garment may be washed in the ordinary way without injury to the marking.

It should be noted that steel pens must not be used with metallic marking inks or the silver will be precipitated on the nib, some of the steel of which will dissolve to take its place. Not only do the marked letters thus become paler, but often acquire a rusty edging due to the presence of oxide of iron. A quill should always be used. It will be blackened the first time it is used with a silver ink, and browned with a gold ink, but subsequent employment of the same pen will not entail any further loss to the ink, especially if the pen is rinsed in soft water each time it is used.

Ammoniacal Silver Ink.

If ammonia solution is added to a solution of nitrate of silver in water, a precipitate of silver oxide is at first formed, but soon dissolves if more ammonia is added. In this way we get a solution which always remains clear and deposits no sediment, whilst the non-ammoniacal silver inks always give a black deposit of silver on keeping, and thus gradually become so weak as to be useless.

Normal Ammoniacal Silver Ink.

Nitrate of silver	6
Gum arabic	6
Sodium carbonate	8
Distilled water	15
Ammonia	12

Dissolve the nitrate in the water in a stoppered bottle, then add the ammonia, and finally the gum and the sodium carbonate. The bottle is then heated in hot water till the colour of the liquid is so dark that it will write legibly. The stopper is left out during the heating. Care must be taken not to overheat, or so much ammonia will be lost that the ink will precipitate. For the same reason the bottle containing the finished ink must be kept well stoppered, and on account of the action of light on silver inks and metallic inks in general, must also be kept in the dark. The foregoing ink is particularly suitable for writing and drawing with the pen. If it flows too thinly, add more gum to it.

Silver Stamping Ink.

Nitrate of silver	10
Ammonia	20
Sodium carbonate	20
Gum	25
Water	80

Dissolve the silver in the ammonia, and the sodium carbonate and gum in the water. Then mix the two solutions, and heat till the liquid, which is at first turbid, becomes perfectly clear and of a fine brown colour. For use with the pen the ink is now ready, but for use with a stamp the amount of water added should be less, so that the ink may be thicker and give sharp letters with the stamp.

For large establishments in which the weekly washing is heavy, such as hotels, hospitals, etc., there is no better marking ink than this. With the stamp especially, it gives the finest lines and details with great distinctness and durability with a very moderate amount of pressure.

Cheap Silver Ink.

The silver inks already given are somewhat dear, as the nitrate of silver must be used in the form of concentrated solution in order to get a deep black writing. But if we combine the silver salt with copper salts a dark black can be obtained without much silver.

When ammonia is added to a solution of a copper salt we get first a pale blue precipitate of hydrated oxide of copper, which dissolves in an excess of ammonia, forming a magnificent dark blue solution. If writing done with this ink is heated, say with a flat iron, a deep black results from the formation of black oxide of copper.

Hence, if we make ink of a mixture of the silver and copper compounds in ammonia, we can get a black and durable writing with a comparatively small amount of silver. Take

Nitrate of silver	15
Sulphate of copper	35
Ammonia	50
Gum	20
Sodium carbonate	20
Soft water	80

Dissolve the metallic salts in half the water, and add the ammonia to the solution. If the amount of ammonia above indicated does not give a clear solution, add more till the liquid is clear. The gum and sodium carbonate are next dissolved in the rest of the water, hot, and the two solutions are then mixed. This ink is of so dark a blue that no dye need be added to it. It is excellent for linen and white silk and wool. For thin fabrics the amount of gum must be somewhat increased.

It may be mentioned here that when a marking ink containing gum and sodium carbonate is used, no preliminary preparation of the fabric is needed.

Silver Drawing Ink.

For drawing on fabrics with silver ink, it is advisable to make the inks from special recipes, to ensure the production of the finest lines. The same recipes also give excellent stamping inks.

Nitrate of silver	20
Soda carbonate	30
Water	100
Tartaric acid	7
Litmus	5
Gum	40

Dissolve the nitrate of silver in 40 of the water and the sodium carbonate in the remaining 60, and add it to the silver solution as long as a precipitate of carbonate of silver is formed. This white precipitate is filtered off, washed on the filter with distilled water, and ground up in a mortar with some water and the tartaric acid. The mass effervesces owing to the escape of carbonic acid. Ammonia is now added cautiously to dissolve the tartrate of silver, and the litmus is next added; it turns the ink blue. The gum in solution is now mixed in, and the finished ink is diluted with water, if necessary. Water-soluble blue can be substituted for the litmus, the object of either being to make the writing legible from the first.

Red Silver Drawing Ink.

Nitrate of silver	48
Tartaric acid	60
Gum	40
Carmine	2
Water	80

Rub the nitrate of silver and the tartaric acid together in a perfectly dry state and then add the ammonia to them, using no more, however, than will give perfect solution with frequent stirring. The clear solution is mixed with the gum in solution and diluted, if necessary, with water.

Kindt's Green Silver Ink.

Nitrate of silver	11
Ammonia	22
Sodium carbonate	22
Water	12
Gum	50
Sap green	2

Dissolve the silver salt in the ammonia and the sodium carbonate in the water separately. Boil the latter and pour the silver solution into it. Then add the gum, and colour with the sap green.

In the author's experience the following process is better: Dissolve the silver salt in the ammonia, and add next the dry sodium carbonate, and finally the sap green and the gum.

This ink only gradually blackens in the light, but the blackening can be hastened by ironing the dry writing.

Chloride of Silver Ink.

A.

Nitrate of silver	8
Water	80
Gum	16
Indigo-carmine	2

B.

Common salt	2
Gum	5
Water	10

These solutions are made and kept separate. The fabric is prepared with B, and when dry is written on with A. When the writing is dry, it is exposed to the sun, and soon turns a deep black by the action of the light on the chloride of silver formed from the nitrate by the common salt.

B.—Gold Inks.

Gold, which is very easily separated in the metallic state from any of its compounds by organic matter, can be used with great advantage for marking inks. With it we can get at pleasure black characters, characters with a metallic lustre, or of a splendid purple colour. The markings are very difficult to efface, and it is unfortunate that the cost of such inks should be so great.

Black Gold Ink.

Reade recommended a process for preparing a gold ink containing ammonium iodide. According to his recipe, however, that salt is made in a way that entails great risk of the formation of iodide of nitrogen, which is very dangerous on account of its great explosiveness. A method of preparing the iodide which involves no such danger, however, is to saturate ammonia with sulphuretted hydrogen made by dissolving ferrous sulphide in dilute sulphuric acid. The iodine is put into the ammonium sulphide so prepared, and dissolves with precipitation of sulphur, so that the liquid becomes turbid. The colourless solution of ammonium iodide is filtered off from the precipitated sulphur, and more iodine is dissolved in it. Gold leaf is now dissolved in the saturated solution, whereby a solution of the double iodide of gold and ammonium is obtained. When used as an ink this solution gives brownish-black letters, which can be made quite black by mixing the ink with one of the foregoing ammoniacal silver inks.

Purple Gold Ink.

This consists of two separate liquids. A is used for the preparation of the fabric, and B for the subsequent writing.

A.

Tin salt	2
Water	200
Gum	20

B.

Chloride of gold and sodium	2
Water	20
Gum	2

Dissolve gold in strong hydrochloric acid by adding the necessary amount of nitric acid in small portions. The usual amount of nitric acid required is one-quarter of the weight of the hydrochloric acid. The impure gold solution containing copper is evaporated nearly to dryness to get rid of the excess of acid, diluted with water, and treated while warm with a solution of oxalic acid, which throws down a brown precipitate of metallic gold. This is washed, and again dissolved in *aqua regia*. Common salt is added to the solution, which on evaporation gives crystals of the double chloride of gold and sodium. By writing on the fabric previously prepared with solution A, purple of Cassius is formed. The tint may be made as delicate as desired by using the solutions in a sufficiently dilute state.

Gold Ink with Metallic Lustre.

Here again two solutions are used—A for the preparation of the fabric, and B for the subsequent writing.

A.

Oxalic acid	2
Gum	4
Water	10

B.

Chloride of gold and sodium	2
Gum	4
Water	20

When the writing appears the fabric is ironed and then washed.

C.—PLATINUM INKS.

When platinum is dissolved in *aqua regia* (the above-mentioned mixtures of 4 parts hydrochloric and 1 part nitric acid) and the solution is evaporated, a residue of tetrachloride of platinum is left. If this is used alone for writing on linen a dead black writing is obtained, but if the fabric has been prepared with tin salt the characters will be red. As before, A is the preparing, B the writing liquid.

Platinum Ink, No. 1.

A.

Oxalic acid	3
Gum	3
Water	10

B.

Tetrachloride of platinum	2
Gum	4
Water	20

As soon as the writing is dry and quite distinct, wash the marked place thoroughly.

Black Platinum Ink, No. 2.

A solution of platinic chloride is treated with a few drops of glycerin (to prevent the ink drying during the writing), and used as the marking ink. On then holding the marked place over a small basin in which a little mercury is heated, the mercury vapour reduces the platinum chloride, and the characters appear in deep black. As they are composed of metallic platinum, which is soluble only in *aqua regia*, this ink can also be used for producing really indestructible writing on paper.

Black Platinum Ink, No. 3.

A platinum ink particularly suitable for marking fabrics for the laundry can be prepared as follows : The portion of the fabric to be marked is treated with a solution of 3 parts of sodium carbonate and 3 parts of gum in 12 parts of water, and allowed to dry. The writing is then done with a solution of 1 part of platinic chloride in 16 parts of water, and, after drying, the characters are moistened with a solution of 1 part of stannous chloride in 4 parts of water. The writing then appears in deep black characters, which penetrate some depth into the fabric.

D.—Vegetable Marking Inks.

As above stated, several organic bodies can be used for making marking inks, and their use is to be preferred to that of metallic salts, as the inks are not only cheaper but are also, under certain conditions, more durable. Writing done with gold, platinum, or silver salts can be gradually but completely effaced by careful treatment with cyanide of potassium or dilute acid.

It would be very easy to get any colour on a fabric with organic matter. All that is required is to mordant the fabric with alumina or tin salt, and then to write on it with a solution of the organic dye, such as cochineal, madder, logwood, etc. The result is that the characters appear in the form of a coloured lake. For fabrics which have not to be wetted, advantage is taken of this principle in producing designs, and it is known as textile printing, but the method does not answer for marking, as the soap and other substances used in washing clothes rapidly destroy the writing.

Of organic matters which will give an ink that will stand washing, the most important are indigotine, aniline black, and the colouring matter of *Semecarpus anacardium.*

Indigotine Marking Ink.

Indigotine, the blue colouring principle of indigo, has the property of being convertible into a colourless substance called indigo white. This substance, however, rapidly becomes indigotine again when exposed to the air, by absorbing oxygen. Indigotine will not dissolve in anything but fuming sulphuric acid.

Indigo white may be prepared by the following recipe :—

Gum	40
Finest powdered dry indigo	40
Ferrous sulphate	80
Sodium carbonate	80
Water	400
Litmus	2

Mix the indigo and the sulphate in a bottle, and then pour in the sodium carbonate dissolved in the water. Cork the bottle lightly, and leave it for several days, shaking it occasionally. When all blue colour has disappeared the reaction is finished. Then place the gum and litmus in another bottle, in the state of very fine powder, rapidly pour the indigo white upon them, and then cork the bottle immediately. When the gum has dissolved the ink is ready.

Use it by dipping a pen into the bottle and writing on the fabric, which need not be specially prepared, and cork the bottle again quickly. The writing soon turns green and finally blue, and can only be destroyed by nitric acid or chlorine. The ink in the bottle gradually forms a deposit of indigotine, which can be used for the preparation of more indigo white.

Anacardium Marking Ink.

There are two sorts of marking-nuts on the market, one from the Asiatic tree *Semecarpus anacardium*, the other from the American *Anacardium occidentale*, the cashew nut. The fruits of the former are heart-shaped, flat, and grey or black in colour ; those of the latter are oval, greyish green, and very lustrous. The colouring matter of both is partly of the nature of an essential oil, partly of a resin. It can be extracted from the crushed nuts with alcohol and ether, but better by means of petroleum spirit, by shaking the mixture in a well-stoppered bottle. The solution is finally filtered into a dish, where it is allowed to evaporate spontaneously to a syrup, under a sheet of paper, so that no dust can get in. The resulting extract is thick enough to be used with a pen or a rubber stamp without any gum. The letters are at first brown, but are quickly changed to a deep black by alkalies. To fix and bring out fully the colour the place marked should be held for a short time over the surface of some ammonia, the alkaline fumes from which rapidly produce the desired result. The writing will then resist washing, even when chloride of lime is used, and also dilute nitric acid.

Black Copper Marking Ink.

Completely precipitate a solution of chloride of copper with one of potassium hydroxide. Pour off the supernatant liquid and dissolve the precipitate in the smallest possible quantity of ammonia. Then add enough dextrin to enable characters which will not run to be written with a quill. When the writing is dry iron it, and it will turn black.

Aniline Marking Ink.

Aniline black makes a most excellent marking ink. The use of other aniline dyes for marking purposes, although beautiful colours are obtained, is inadvisable, on account of the want of permanence displayed in the majority of cases by the writing. The coloured aniline marking inks are especially fugitive with alkali, the very agent with which they are brought into contact in the laundry. The following are some of the best of the known recipes for aniline marking inks.

Copper Aniline Marking Ink.

This consists of two solutions, which are not mixed until just before use.

A.

Chloride of copper	15
Sal ammoniac	10
Sodium chlorate	20
Water	100

B.

Aniline hydrochloride	25
Gum	20
Glycerin	5
Water	50

For use a small quantity of A is mixed with five times its weight of B. The result is a green liquid which turns black in a short time, and is then unfit for use. As it is, the ink has to be fixed on the dried fabric, at once, by holding it over boiling water until it is thoroughly soaked. No washing with soap will then efface the writing, which even resists chloride of lime for a long time.

Jacobson's Marking Ink.

This also consists of two liquids, which are mixed just before use, A being added to four times its weight of B.

A.

Crystallised copper chloride	85
Sodium chlorate	106
Sal ammoniac	53
Distilled water	600

B.

Glycerin	30
Gum	20
Dissolved in water	40
Aniline hydrochloride	60
Dissolved in water	90

The ink is green at first, but the writing soon turns to a black which is fast to washing. This ink is known as Jetotine.

Aniline Stamp Ink.

This again is a two-fluid ink. For use B is mixed with four times its weight of A. The writing must be fixed by leaving a hot iron on it for a few minutes.

A.

Chloride of copper	1
Ammonia	40
Common salt	1

B.

Aniline hydrochloride	40
Gum	15
Glycerin	15
Water	30

Black Aniline Marking Ink.

Aniline black	1·75 grammes.
95 per cent. spirit	42·0 ,,
Hydrochloric acid	60 drops.
Gum arabic	2·5 grammes.
Water	170·0 ,,

The aniline is first ground up with the spirit and the acid. The gum is then rubbed in after being dissolved in the water. The result is an intensely black ink, which, however, is easily washed out. In order to be able to use it for marking clothes requiring washing, 2·5 grammes of shellac must be substituted, dissolved in 170 of spirit for the gum solution.

This ink can also be used for writing on wood, glass, metal, leather, and india-rubber, and is unaffected by water.

Since the discovery of the aniline marking inks the demand for the much more expensive metallic marking inks has been greatly reduced, but the latter still deserve the preference so far as resistance to the alkalies used in washing is concerned. To these they are quite unsusceptible, so that the writing can never disappear. They can be completely effaced, however, by solution of cyanide of potassium, and writing done with silver inks can be destroyed with very dilute nitric acid. Gold and platinum can only be effaced by solutions which contain free chlorine.

A writing which is absolutely indelible can be obtained by writing on the fabric with a fine glass point wetted with concentrated sulphuric acid. The instant the writing turns brown, the marked place is thoroughly rinsed. In this way a part of the fibre is carbonised, and a permanent marking is secured, but this method is obviously unsuitable for general use.

XXXIV.

STENCIL INKS.

Liquid.

A GOOD stencil ink for wooden cases, etc., is made by grinding ivory black (bone black), tinted with a little ultramarine blue, into a good copal varnish or other drying medium, and thinning the mass with turps or white spirit to the right consistence for application with the stencil brush.

Solid.

A black, soluble stencil ink for marking chests and bales is made by allowing 80 parts of good glue to swell up in water for twelve to twenty-four hours, and then dissolving it, on a water-bath, in 450 parts of fresh water, along with 16 parts of yellow commercial dextrin, 6 of sugar, 22 of glycerin (crude, 28° B.), and 26 of water-soluble nigrosine. The solution is next incorporated, by stirring, with 400 parts of lampblack, to form a paste, which is then thickened by further heating on the water-bath, until a small sample is found to set hard on cooling. All the superfluous water being thus evaporated, the mass is pressed in greased moulds. The addition of a little ox-gall will help the ink to run freely when used on greasy material.

BLUE INK FOR GALVANISED WARE, ETC.

Dissolve in 1 gallon of water 1 lb. of shellac, ¼ lb. of borax; then stir in the requisite quantity of ultramarine blue.

XXXV.

INK SPECIALITIES.

CERTAIN industries require special liquids with special properties for writing on such materials as metal, leather, wood, ivory, etc.

INK FOR METAL.

Lustrous Black Ink for Metal.

Copal	10
Oil of turpentine	12
Lampblack	2

The copal is melted in an iron pot, and then further heated till dense fumes come off, and the copal begins to decompose. The cover of the pot is kept ready, in case the copal should catch fire. When the copal has wasted down to about four-fifths of its original weight, the pot is allowed to cool a little, and the turpentine gradually stirred in, and finally the soot. Care must be taken that the pot is not too hot when the turpentine is put in, or it will be thrown out again. The finished mass is thinned with more oil of turpentine, if necessary, until suitable for writing. The ink must be kept in well-closed bottles, as it dries up quickly.

This ink can be used for writing upon any metal, and the writing adheres best when the surface is quite clean and somewhat rough. It should be sand-papered before the ink is applied.

Lustrous Red Ink for Metal.

Copal	20
Oil of turpentine	24
Cinnabar	2

Proceed as directed under the last recipe, except that less turpentine must be used, as the ink must be kept thick enough to prevent the cinnabar, which is very heavy, from settling.

Lustrous Coloured Inks for Metals.

By substituting other pigments, such as ultramarine, Prussian blue, chrome-yellow, aniline violet, etc., for the cinnabar in the last recipe, ink of any desired colour may be made.

Dull Black Ink for Metals.

Copper sulphate	10
Vinegar	2
Gum	4
Lampblack	2
Water	10

Fine dead black writing can be done on clean iron, zinc, or brass with this ink, but not on copper or tin. For these two metals ink made by the following recipe may be used :—

Sulphate of copper	10
Hydrochloric acid	4
Sal ammoniac	8
Lampblack	2
Gum	4
Water	10

Ink for Writing on Silver.

Dissolve the double chloride of gold and sodium in fifteen times its weight of water. The solution writes a beautiful golden brown on silver. If this colour is to remain, the silver is dipped into ammonia and rinsed. If the writing is exposed to the sun instead, the colour soon passes into black. Black writing on silver can also be executed with a solution of tetrachloride of platinum made as above directed. If we follow engraved lines on the silver with this ink, the effect known as *niello* is produced.

Black Ink for Zinc.

Sulphate of copper	2
Potassium chlorate	2
Water	72

On using this solution with a quill the writing is at once black. When dry, rinse with water, and go over the letters with an oiled rag.

Black Ink for Leather.

This consists of two separate fluids. The place to be written on is painted over with A, allowed to dry, and then written on with B. The ink writes a fine black, and penetrates deeply, especially if the back of the leather is wetted before the ink is applied to the other side.

A.

Galls	20
Gum	2
Water	200

B.

Ferrous sulphate	4
Gum	8
Indigo carmine	2
Water	40

Black Ink for Linen, Cotton, Wool, and Silk.

The place to be marked is prepared with solution of alum, and then, when dry, with decoction of galls. It is written on with the solution marked B in the last recipe. A slight increase in the amount of indigo carmine makes the writing more permanent.

Waterproof Blue Ink for Glass.

Bleached shellac	10
Venice turpentine	5
Oil of turpentine	10
Powdered indigo	5

Dissolve the shellac and the Venice turpentine in the oil of turpentine over hot water. Then stir in the indigo.

Laboratory Ink.

Nigrosine	10
Ruby shellac	20
Borax	30
Ammonia	15-30
Water	400

Boil the shellac and the borax in the water till both are dissolved. Then filter, and add the nigrosine and the ammonia. This ink resists laboratory fumes for a long time.

Ink for Ivory.

It is possible not only to write indelibly in black on ivory, but also by a simple process to execute on the material very beautiful drawings in every shade from the palest brown to the deepest black.

The ivory must be prepared first by soaking it in a strong solution of soap or of ammonia, and then rinsing. In the meantime a normal ink is made by dissolving nitrate of silver in ten times its weight of water. The solution is divided into ten equal parts. One is left as it is, the second is diluted with its own volume of water, the third with twice its own volume of water, and so on, so that the last is diluted with nine times its volume. The weaker the solution the paler it will write on the prepared ivory, the tint ranging from a deep black to a very light grey. By judiciously using these inks drawings can be executed on ivory, either with brush or pen. They are indelible, and may contain all the ten shades together. If the drawing is to acquire a warm brown-gold colour the ivory is laid in a 1 per cent. solution of the double chloride of gold and sodium. As soon as the desired colour has appeared, the ivory is removed, rinsed, and immediately put into a 10 per cent. solution of sodium thiosulphate.

Ink for Writing and Drawing on Wood.

By skilful treatment drawing may be made on pale wood which produce the effect of inlaid work at a distance. The wood is prepared by painting it over repeatedly with a boiling solution of gelatin, and then with the following mordant :—

Alum	10
Hydrochloric acid	10
Tin salt	2
Water	50

This is applied several times by means of a sponge. It partly serves as a basis for the ink, and partly prevents it from smudging by ensuring its penetration. The following inks are then used, each for the colour named :—

Black.—Anacardium ink, painted over with ammonia when dry.
Brown.—Solution of potassium permanganate.
Blue.—Decoction of logwood.
Red.—Decoction of redwood or ammoniacal cochineal ink.
Yellow.—Decoction of Persian berries, or solution of picric acid.

Ink for Wooden Boxes.

Logwood extract	10
Dissolved in—	
Water	500
Potassium chromate	2

Etching Ink for Metal and Glass.

Copper sulphate	20
Gum	10
Vinegar	5
Lampblack	5
Water	60

An ink for etching glass is also prepared from fluorine compounds. On the addition of a strong acid hydrofluoric acid is liberated, and attacks the glass, producing a matt surface.

Diamond Ink.

One part of ammonium fluoride is made into a thin past with sulphuric acid, and 2 parts of barium sulphate are added to the mixture.

Buchheister's Stable Etching Ink for Glass.

A.

Sodium fluoride	30
Potassium sulphate	7
Water	500

B.

Zinc chloride	14
Salicylic acid (conc. solution)	56
Water	500

The two solutions are mixed immediately before use. Etching inks for glass must be kept in bottles of gutta-percha or of lead, or in glass bottles coated inside with paraffin wax. Care must be observed in handling hydrofluoric acid, for it produces painful injuries on the skin.

XXXVI.

SYMPATHETIC INKS.

THESE have little, if any, practical value, and under normal conditions are simply chemical playthings, although in war time they are used for secret communications.

They are inks which can be made to change, to appear, or to disappear. Some of them are one-fluid inks, and others are two-fluid inks—one fluid being used for writing, the other for developing.

YELLOW SYMPATHETIC INKS.

A.

Dissolve copper in hydrochloric acid containing a little nitric acid, and dilute the solution till writing done with it ceases to be visible. On heating the paper the letters appear, of a yellow colour, and disappear again on cooling.

B.

Dissolve antimony in hydrochloric acid containing a little nitric acid, and write with the solution. If the dry writing is painted over with decoction of galls the writing becomes visible, of a yellow colour.

SYMPATHETIC GOLD INK.

If paper is written on with a not too dilute solution of the double chloride of gold and sodium, the writing appears permanently on treatment with a 10 per cent. solution of oxalic acid. By ironing the paper a fine metallic lustre can be given to the characters.

Red Sympathetic Ink.

This is a two-fluid ink. The writing is done with a very dilute solution of the double chloride of sodium and gold, and when the paper is dry the hitherto invisible characters are developed by sponging them over with a solution of tin salt, when purple of Cassius is formed. If the paper is first prepared with tin salt the purple will appear at once. In a similar manner all two-fluid sympathetic inks can be used to produce a writing visible from the first.

Disappearing Purple Ink.

Write with a very dilute solution of iron in *aqua regia*, and shut up the paper with a watch glass containing thiocyanate of potassium and a little sulphuric acid. The writing soon becomes visible, of a blood-red colour, but if held over ammonia will disappear again completely.

Green Sympathetic Ink.

A one-fluid ink is made of a mixture of cobaltous and nickelous nitrates. The characters are scarcely visible when dry, but on heating they appear of a beautiful green, which disappears again on cooling. By varying the proportions of the two salts different shades of green can be obtained.

Two-fluid Green Sympathetic Ink.

Write with a solution of chlorate of sodium, and when the writing is dry go over the paper with a sponge wet with solution of sulphate of copper. The writing will at once appear permanently, and of a bright green colour.

Blue Sympathetic Ink.

Many cobalt salts form crystals which are red at ordinary temperatures, but turn to a full blue on heating. Hence any soluble cobalt salt can be used as a sympathetic ink. Those most used are the chloride and the nitrate. The characters are almost invisible at ordinary temperatures, but appear of a distinct dark blue when heated, again to disappear on cooling.

The ink that Paracelsus is reputed to have used to draw the leaves of the trees in a landscape, the rest of the drawing being executed with ordinary pigments, was probably a cobalt preparation, although cobalt was not recognised as a metal until long afterwards. Tradition says that the drawing had the effect of a winter landscape when it was cold, and of a summer one when it was warmed.

Ink with Cobalt Thiocyanate.

This salt is extremely sensitive to changes of temperature. It gives a pale red writing, which with a very small rise of temperature turns blue. Cobalt thiocyanate is prepared by adding an alcoholic solution of potassium cyanide to a solution of cobaltous sulphate as long as any potassium sulphate precipitates. The filtrate is a solution of cobalt thiocyanate, and is evaporated at a very gentle heat. Writing with it turns blue, even when laid in the palm of the hand.

Brown Sympathetic Ink.

Bromide of potassium	2
Sulphate of copper	2
Water	40

The cold characters are scarcely visible, but turn brown on heating.

Oxalic and Molybdic Ink.

Boil a concentrated solution of oxalic acid, and add to it as much molybdic acid as it will dissolve. Preserve the solution in black bottles. The characters written with it are at first invisible, but exposed to the sun they turn dark blue, and, when heated, black.

Garzino's Blue Ink.

This consists of a solution of a ferrocyanide or ferricyanide, with the subsequent use of a solution of an iron salt to develop the writing. In order to render the characters visible at the time of writing, powdered graphite and magnesium carbonate are added, and after the writing is dry these are removed by means of india-rubber. If copies of the invisible writing are required, gum is added to the ferrocyanide solution, and the copy taken on damp paper by pressure. Both the copy and the original can afterwards be developed by applying the iron solution.

XXXVII.

STAMPING INKS.

THESE are made in various colours, and their manufacture has become an important branch of the ink industry since the introduction of self-inking stamps.

A good stamping ink must give a clean impression, and must not dry quickly on the stamp, so as to fill the die and make the impression indistinct. This is of especial importance with india-rubber stamps, as such stamps cannot be cleaned with a brush, which would destroy the sharp outlines of the letters and make the stamp useless.

Ordinary printers' ink has been much recommended as a stamping ink, and is excellent for the purpose, except for one thing. It gives a sharp, black impression which dries very quickly on the object stamped, but the ink dries almost as fast on the stamp. This may be remedied, however, by dilution with one-tenth to one-sixth of its volume of filtered linseed oil. Too much of the oil must, however, not be added, for it will not only make the ink too thin and pale, but will cause the impression to be surrounded with a transparent, greasy border.

BLACK STAMPING INK.

Finest lampblack	10
Gum	4
Glycerin	4
Water	3

Dissolve the gum in the water, add the glycerin, and grind the mixture up intimately with the lampblack. The glycerin, which is thick but not greasy, absorbs moisture from the air, and so keeps the ink liquid. For very finely engraved stamps the proportion of black is increased, to make the ink rather thicker. This excellent ink will not run, and gives very sharp impressions.

Coloured Stamping Inks.

These are obtained by replacing the lampblack in the last recipe by other pigments, according to the colour desired, such as chrome-yellow, red lead, ochre, green cinnabar, green ultramarine, indigo, ultramarine, Prussian blue, red ochre, umber, etc.

Aniline Stamping Inks.

Very beautiful stamping inks can be made with the coal-tar colours, but some skill is required in their preparation. The manufacture is simple enough if the dyes are used in the solid form, for they have merely to be ground up to a uniform mass with glycerin and mucilage. If, however, they are to be used in solution, it must be a concentrated solution in the strongest spirit. To this solution glycerin is first added, and the gum is put in last, and very gradually. It is also a good plan to replace from a quarter to a third of the gum by sugar.

Soluble Stamping Inks.

Since the discovery of aniline dyes soluble in water the manufacture of excellent stamping inks has become very simple with their aid. The best to use is water-soluble blue. This is made into a syrup with glycerin. This syrup is applied with a brush to a smooth, soft pad, and rubbed in uniformly with a wooden spatula. A single application to a small pad of about 8 square inches area is enough to enable a rubber stamp to produce hundreds of impressions. The composition of the ink depends on whether it is to be placed on a pad or is to be used for filling a soft inking stamp. In the first case it must be thick, so that enough may adhere to the stamp to give a good impression. In the latter case, when the ink has to pass through a filter to the stamp from a reservoir, it must be more fluid, so that it will pass through fast enough to allow the stamp to be quickly used many times.

Dieterich's Stamping Inks.

Aniline soluble blue	3
Dextrin	15
Water	15
Glycerin	70

For inks of other colours, the following dyes may be used :—

Violet	2	parts of	methyl violet.
Blue-red	2	,,	diamond fuchsine.
Bright red	3	,,	eosine.
Green	4	,,	aniline green.
Brown	5	,,	vesuvine.
Black	3	,,	phenol black.

Indelible Stamping Ink.

Many textile manufacturers mark their goods in such a way that they can be washed, bleached, and dyed without affecting the marking.

One body only is known which resists all chemical reagents entirely, namely, carbon. Hence an indelible stamping ink must contain that pigment. The best is ordinary printing ink diluted with one-quarter of its volume of good boiled linseed oil, which makes it penetrate deeply into the fabric and become absolutely indelible. All known bleaching agents leave it quite unchanged. It can, it is true, be hidden by dyeing the fabric, but then, if the dye is destroyed with chlorine water or very dilute *aqua regia*, the marking shows up with perfect distinctness.

Laundry Stamping Ink.

Silver nitrate (5 parts) is dissolved in ammonia (10 parts); another solution is prepared containing 5 parts of gum arabic and 7 parts of crystallised sodium carbonate in 12 parts of distilled water. The two solutions are mixed for use, and the stamping heated.

Dieterich's Laundry Stamping Ink.

Silver nitrate	25
Gum arabic	25
Ammonia	60
Lampblack or indigo	2·9

The ink is distributed on a glass plate, and used with the ordinary rubber stamp.

Stamping Inks for Meat.

Ink intended for stamping meat should contain only ingredients that are insoluble in water and do not alter on pickling the meat. The ink patented by A. Leonhardi (German Patent, 105,107) answers to these requirements. It is prepared from the so-called oil-soluble dyes, which are dissolved in benzene, petroleum spirit, etc. The following is a typical recipe:—

Oil-soluble dye	5 to 20 per cent.
Rosin	5 ,,
Petroleum spirit	75 to 90 ,,

The inks, which are usually blue or black, are applied to the meat by means of rubber stamps.

SCHMIDT'S STAMPING INK.

The ordinary indelible stamping inks, consisting in the main of lampblack and boiled linseed oil, can only be removed with difficulty and at the best incompletely, since although the oil medium can be removed by means of solvents, the lampblack resists all chemical treatment. Hence such paper cannot be re-pulped for the manufacture of white paper. To avoid this, the lampblack in stamping ink (and in printing ink) has been replaced by other black pigments, which can be removed from the paper by chemical processes.

The pigment used for this purpose is manganese peroxide, either in the form of the naturally occurring mineral (manganite, etc.) or as obtained in large quantities as a by-product in certain chemical factories (soda works). One method of preparing an ink from this pigment is as follows: Forty parts of the manganese peroxide are finely ground with 60 parts of boiled linseed oil, or one of the substitutes for that oil used for printing inks (oleic acid, oil of turpentine, glycerin, rosin soap, etc.). The usual additions to obtain a definite colour tone (nigrosine, etc.) may also be made, just as in the ordinary printing inks.

To remove the printed or stamped characters done with this ink, the paper is treated with hot or cold aqueous solutions of alkali hydroxides or carbonates, the solution of the oily medium thus separated is drained off, and to remove any manganese left the pulp is treated with sodium sulphite, and then with acid, either in the form of liquid or of vapour. Hydrochloric acid is particularly suitable for this purpose, since it reacts with any residual traces of manganese dioxide to form chlorine, which has a bleaching action upon the pulp.

XXXVIII.

LAUNDRY OR WASHING BLUE.

It is well known that in laundry work the last rinsing water is mixed with a little blue to neutralise the yellow tinge of the linen and make it a pure white. Many blues are put on the market for this purpose, such as smalts, Prussian blue, sulpho-indigotic acid and indigo carmine, both in a solid state and as solutions.

It is easy to see that solutions of colouring matter are preferable to solid powders, as they can reach the interior of the fibre, whilst the powders can only adhere mechanically to the outer surface.

A.—Insoluble Laundry Blue.

Smalts.

Smalts or eschel is a blue glass. It is made by fusing cobalt ores with potassium carbonate and quartz. The glass is ground and levigated with the greatest care. Smalts is thus obtained in several different degrees of fineness and shade of colour.

When smalts is used as a laundry blue it must be carefully mixed uniformly with the starch, which makes it adhere to the garment. There is a powdered washing blue on the market which is an intimate mixture of smalts and starch. When used in the laundry it is boiled with water.

Prussian Blue.

This has already been spoken of several times in this book. It is dark blue with a coppery shade, and the darker sorts are called Paris blue.

By making Prussian blue for oneself and leaving the wet precipitate for some hours in strong nitric acid, a product equal to the best Paris blue is obtained.

Prussian blue, like smalts, can only be used in combination with starch or gum. It has a very intense colour, so that care must be taken that it does not make the linen look blue instead of white.

A great drawback to the use of Prussian blue as a washing blue consists in the fact that linen on which it has been frequently used gradually assumes a yellow tinge, owing to the action of the washing soda and soap on the Prussian blue, which results in the slow formation of brownish-yellow oxide of iron on the fabric.

B.—Soluble Laundry Blue.

Soluble Prussian Blue.

This is prepared for laundry purposes exactly as for ink making. It can be poured into the water in which the linen is rinsed, and need not be mixed with starch or gum.

Although the soluble Prussian blue has the same drawback as that just mentioned as attaching to the ordinary pigment, it has it to a much smaller extent, as the oxalic acid in which the blue is dissolved has also a solvent action on the oxide of iron.

It may here be mentioned that iron-moulded linen can be made perfectly white again by twenty-four hours' immersion in one-tenth per cent. solution of oxalic acid in distilled water.

Indigo Laundry Blue.

These are the most to be recommended of all washing blues, as they do not injure the washing in any way, are all freely soluble in water, and adhere very uniformly to the linen. They are used either as sulpho-indigotic acid, which is only employed in solution, or as indigo carmine, which may be used as a powder, as a paste, or in solution.

Sulpho-indigotic Acid.

This is easily made by thoroughly drying powdered indigo, and then stirring it up with twice its weight of fuming sulphuric acid. The mass, which gets very hot, is well stirred with a strong glass rod, and then left to stand for twelve hours. The whole is then put into a funnel plugged with asbestos, through which the solution of sulpho-indigotic acid drains. It will be so strong as to look quite black. The insoluble residue on the filter should be rinsed with water, and the rinsings allowed to mingle with the rest of the filtrate. The washed residue is again dried, and serves for the production of more sulpho-indigotic acid with a fresh lot of ingredients. It is of great importance that in each operation the indigo should be in excess of the sulphuric acid, so that none of that acid can be present in the solution of the sulpho-indigotic acid. Such an excess would have a most destructive effect upon the garments. The solution of sulpho-indigotic acid may be bought concentrated under the name of "indigo washing blue essence," or diluted, as "indigo washing blue." A few drops of the "essence" are sufficient for a large washing tub of water.

Indigo Carmine.

The preparation of this substance has already been described. We have, therefore, only to say a few words about the various forms in which it comes upon the market.

The paste form, although highly concentrated, is not favoured by the laundry trade, as it is so difficult to avoid taking too much of it, and so making the linen blue. The solution is sold in different degrees of concentration as "indigo carmine essence" and "indigo carmine washing blue." The essence is made by adding to the paste just enough water to make a solution. It looks quite black, except in very thin layers indeed.

Solid Indigo Carmine Laundry Blue Tablets.

Indigo carmine is triturated with sufficient potato starch to make a thick paste which is rendered homogeneous by beating it with a block of wood and mixing on a stone slab, and is then pressed into moulds similar to those used in making water-colour tablets. The cakes are detached by tapping the moulds, and are placed in a warm room to dry, being turned over repeatedly and left until they have acquired a surface gloss and no longer colour the fingers when touched. For use, the tablets are placed in water, in which they fall to pieces, producing a blue solution with a deposit of starch. They may also be boiled in water, in which case the starch thickens, and the resulting dark blue paste can then be easily distributed in water.

Frothing Laundry Blue.

A water-soluble aniline blue (74 parts) is mixed with oxalic acid (36 parts), and the mixture is added to an equal quantity of a mixture of 160 parts of sodium bicarbonate, 50 parts of tartaric acid, and 85 parts of citric acid. The mass is then heated and compressed into tablets.

Compressed Laundry Blue.

Finely powdered ultramarine and acid-free indigo carmine (or a blue aniline dyestuff or mixture of dyes) are intimately mixed with a substance that will yield carbon dioxide, and compressed into tablets. A suitable mixture for this purpose is sodium bicarbonate with a suitable organic acid. The complete mixture is thoroughly mixed with alcohol, and then dried and compressed into the desired form. This laundry blue dissolves readily in water, and suddenly produces a froth. The addition of a little talc facilitates the separation of the mass from the moulds and gives a polished surface to the tablets, etc.

Glossy Laundry Blue Paste.

Four kilos of the best glue are finely divided (or glue powder may be used) and allowed to stand for twenty-four hours in 12 litres of cold water, after which the mixture is heated in a steam-jacketed boiler or on a steam bath until solution of the glue is complete. In another vessel 25 kilos of dextrin are dissolved in 25 kilos of hot water, and the solution is mixed with the solution of glue, after which 60 kilos of ultramarine, previously mixed with 25 kilos of glycerin, are added, and the whole is ground up in a mill. A little aniseed oil is added to mask the odour of the glue, and the finished product is put into tin canisters, in which it solidifies to a jelly.

Solid Laundry Blue from Aniline Dyes.

From 5 to 15 kilos of alkali blue R are dissolved in 500 litres of water which is heated in a large vat with naked steam, the mixture being constantly stirred. When solution is complete sufficient caustic soda lye is added to cause the blue colour to disappear, after which 250 kilos of light spar are introduced, followed, after thorough admixture, by a measured quantity of hydrochloric acid in sufficient quantity to redden litmus paper. If the blue colour then re-appears, it is an indication that the dyestuff has been precipitated on the light spar, i.e. has formed a lake similar in its shade of colour to ultramarine blue. The precipitate is allowed to settle, is then collected in a straining bag or in a filter press, and is dried at a moderate heat and ground up as finely as possible.

THE END.

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