THE

# MANUFACTURE OF INK:

#### COMPRISING

THE RAW MATERIALS, AND THE PREPARATION OF WRITING, COPYING, AND HEKTOGRAPH INKS, SAFETY INKS, INK EXTRACTS AND POWDERS, COLORED INKS, SOLID INKS, LITHOGRAPHIC INKS AND CRAYONS,

PRINTING INK, INK OR ANILINE PENCILS, MARKING INKS, INK SPECIALTIES, SYMPATHETIČ INKS, STAMP AND STENCIL INKS, WASH-BLUE, ETC. ETC.

TRANSLATED FROM THE GERMAN OF

SIGMUND LEHNER, CHEMIST AND MANUFACTURER.

WITH ADDITIONS BY

WILLIAM T. BRANNT, EDITOR OF "THE TECHNO-CHEMICAL RECEIPT-BOOK."

#### ILLUSTRATED.

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## $\mathbf{PREFACE}.$

THE use of few chemical preparations has become so general as that of ink, and its manufacture is one of the most promising of the small industries, there not being many articles of daily requirement which, from a small investment, yield so large a profit.

The lack of a recent treatise in the English language containing detailed descriptions of the raw materials and receipts for the preparation of ink, and the apparent necessity, as shown by frequent inquiries, for such a volume, were the considerations which led to the preparation of "THE MANUFACTURE OF INK."

The work upon which it is mainly founded is "DIE TINTEN-FABRIKATION," by Sigmund Lehner, which has met with great success in Germany, it having passed through four editions, and is thoroughly practical. Most of the receipts have been practically tested, so that good results should be obtained if the work is carried on strictly in accordance with the directions given, and raw materials of good quality are used. In case deviations should occur, it should be considered whether the manipulation has been free from mistakes, or—what frequently

#### PREFACE.

happens with the use of extracts of coloring matters whether the quality of the materials is at fault.

Since a detailed account of the required raw materials has been given, and their properties have been accurately and clearly described, with the exercise of some care in buying them, and a strict observance of the directions given, good results should invariably be obtained.

It is hoped that the additions made here and there by the translator, as well as the chapter on "PRINTING INK," added by him, may contribute to the usefulness of the treatise.

Finally, it may be stated that the publishers, who desire to cover with their technical publications all of the important branches of industry, have spared no expense in the mechanical production of the book; and, as is their constant practice, have caused it to be provided with a copious table of contents and a very full index, which will render reference to any subject or special receipt prompt and easy.

W. T. B.

PHILADELPHIA, July 1, 1892.

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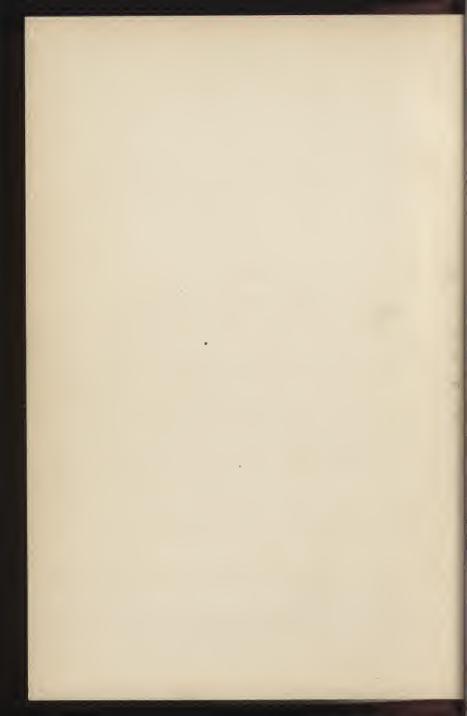
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XV



## THE MANUFACTURE OF INK.

## I.

#### INTRODUCTION.

THERE are few chemical preparations, perhaps none, of which the benefit in civilized life is so great or of which the use is so widely extended, as that of common writing ink; consequently there is no compound, the quality of which it is more necessary to inquire into; and yet there is perhaps no subject which, up to a comparatively recent period, has been more neglected by chemists.

Before Lewis, towards the close of the last century, directed his attention to the subject, no author appears to have particularly applied himself to inquire into the theory of the composition of ink, or to bring it to perfection. All that is to be found in the works of previous writers consists merely of formulæ for various kinds of ink, which, being composed without any attention to chemical laws, were more or less defective, so that it may be truly said, that until the time of Lewis the preparation of writing fluids, the properties of which it is so essential to attend to, was left entirely to chance, or to empirical prescriptions.

It is, indeed, true that some good kinds of ink have been discovered by accident, but, generally speaking, the

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#### THE MANUFACTURE OF INK.

demands formerly made on a good ink were very modest indeed. If it furnished black characters, the fact that after a short time it formed a thick sediment was pardoned; this sediment being considered a necessary property and even the prerogative of a good ink, and the trouble of regularly stirring it up before writing was not begrudged. Hence, a small stick of wood was the constant companion of the inkstand, and belonged to it as a necessary auxiliary apparatus, just as much as the pen for writing.

The ancient inks, according to the opinions of most writers, were similar to the Indian or Chinese ink of today. Pliny and Vitruvius allude to it as a combination of soot or lamp-black with glue or gum; and Dioscorides even mentions the proportions of three of the former to one of the latter.

The art of preparing ink must have been quite fairly known in the middle ages, as is evident from the wellpreserved parchments of that time; characters written six and even eight centuries ago, still showing their pristine blackness.

It would almost seem that the art of ink-making had in the course of time decidedly retrograded, it being frequently found that the characters of manuscripts less than a century old are so faded as to be scarcely legible. It may, however, be remarked that the quality of the paper and the presence of lime and chlorine, even if only in minute quantities, in many papers, may have exerted a destructive influence upon the characters, and the latter if written upon parchment might have been as well preserved as the writings of the monks who, as is well known, were the chief book-writers of the middle ages.

#### INTRODUCTION.

It is considered necessary to make here a few remarks regarding paper. All our bleached papers contain minute quantities of chlorine, and the presence of this substance will in the course of several centuries cause the decay of the paper. It is, therefore, entirely useless to write a document intended for posterity with unchangable ink upon paper. The ink will not fade, but the paper will be reduced to dust. After a few centuries our modern books printed upon paper bleached with chlorine will no longer exist, because of the decay of the paper, this being especially the case with the very cheap wood paper so much used in recent times. Such paper already turns brown in the course of a few years, and becomes so brittle that it breaks in folding, and hence should not be used for documents and books intended for posterity. Upon durable material the printing ink, whose coloring principle is carbon, used for printing such books, would last forever. The linen in which the Egyptian mummies are wrapt is evidence of the durability of unbleached vegetable fibres-hence, also of unbleached paper. In our time, therefore, four thousand years after their preparation, the tissues are only slightly brownish and possess considerable solidity. If the ancient Egyptians had written with good ink upon such tissues, the characters would be legible at the present time.

Although, as previously mentioned, considerable improvements in the composition of inks were made by Lewis and others, in modern times, their preparation has been largely influenced by two factors. One of these factors is the supplanting of the gray or brown handmade paper by the white smooth machine-made paper. The latter can only be obtained by very vigorous bleaching of the raw material, and, hence, always contains small quantities of lime and chlorine. Although the quantitics of these substances in a good paper may be very minute, they are, nevertheless, sufficient to effect, in the course of time, the destruction of some inks and the characters written with them. It must, therefore, be sought to prepare inks of such quality that the writing will be imperishable, notwithstanding these influences.

The second factor which has influenced the compositions used as inks, is the revolution in the tool used for writing. While formerly the goose-quill was exclusively used for writing, and the raven-quill for drawing, steelpens have at present been substituted for both. The horny substance of bird-feathers, however, is very resistant towards chemical influences; while the steel, of which our writing and drawing instruments are made, is readily attacked by different substances, very dilute acids in the ink corroding steel-pens in a very short time.

Prior to the successful manufacture of inks entirely or almost entirely indifferent towards steel-pens, it was sought to overcome this evil by providing the pens with a coating of copper, silver, and even gold. It will be readily seen that such coating can be of but little use, since after writing for a short time, even upon the smoothest paper, the point of the pen is ground down to a certain extent so that the steel is bared at this most important part. Now, by the action of the ink the fine point is corroded, and the pen, in a short time, becomes useless.

The progress in chemistry in modern times has also removed these evils, there being now inks which fullfil all other requirements, and leave the substance of the pen entirely unaltered.

## II.

#### THE VARIOUS KINDS OF INK.

Writing inks, which serve for the production of characters by means of a pen.

Copying inks or inks which, after having been transferred from pen to paper, and having become dry, will communicate a portion of their substance to a sheet of damped paper strongly compressed upon them, thus furnishing two, and in some instances—by renewed application with pressure, of clean moistened paper—even a third or fourth copy of the same manuscript. *Hecto*graphic inks, which permit the repeated copying of the writing transferred to a peculiar basis, may be considered a subdivision of this group.

Ink powders are pulverulent or solid masses, which, when dissolved in water, directly yield ink.

Ink pencils may, in accordance with their constitution, directly follow ink powders. They are a sort of pencils by means of which characters resembling those written with aniline inks may be produced upon slightly moistened paper.

Drawing inks for the execution of drawings with the ordinary pen or drawing pen.

Lithographic inks represent a special kind of ink

which is exclusively used for writing and drawing upon lithographic stones, and must be able to resist certain caustic fluids used in lithographing.

Marking inks serve especially for indelibly marking linen, etc.

Stamping inks for stamping designs to be executed in embroidery upon. stuffs, for moistening stamps used by firms and individuals, etc.

*Ink specialties*, among which may be classed gold and silver inks, as well as sympathetic inks.

*Printing inks*, though differing in their composition from ordinary ink, will also be considered.

As will be seen from this general division, the number of inks and ink-like products is quite large. To give all known directions for making ink would require several volumes; but as a large majority of them are simply empirical prescriptions, only approved receipts, thoroughly tested, will here be given.

Although the preparation of ink would seem a simple operation, it must be confessed that but little is known in regard to the chemical processes taking place thereby.

The majority of the fluids designated inks consist of combinations of metals with various organic substances, among the latter of which the tannins and other certain vegetable extracts deserve special mention. Formerly the opinion prevailed that only one of the substances contained in a tannin caused the formation of the black body which imparts to the ink its properties; but it is now known that a considerable number of chemical combinations, which are only partially understood, occur in the composition called ink. This explains why so many prescriptions for the preparation of inks have

been and are still given; and it also explains the remarkable fact that two prescriptions, identical as to the substances to be used, frequently show extraordinary variations in regard to the quantities of the substances; while one prescription lays particular stress upon the preponderance of one substance, the other demands just the reverse.

From what has been said it will be seen that the manufacturer of inks must still largely depend on receipts; and it is advisable for him to subject every prescription which becomes known to him to a test, and improve his receipts by experiments. That such experiments pay need scarcely be mentioned, because there are few articles of daily use, which are sold at such a large profit as ink.

## III.

#### WRITING INKS.

A GOOD writing ink should possess the following properties :---

1. Intense color, that is, the writing executed with an ink, no matter of what color, should acquire, either at once, or in a short time afterwards, a strongly pronounced color.

2. Fluidity.—The ink must readily flow from the pen, so as to allow of the execution of the finest lines and characters. A useful ink should not be viscous, and when drying on the pen must not form a thick, hard crust. The latter evil is frequently caused by the ink being too concentrated, and may be remedied by the addition of water. If, however, the ink remains viscous after such dilution, it is a proof that either the composition is at fault, or that the ink has been spoiled in consequence of certain processes of decomposition which have taken place in it.

As will be explained later on, the above-mentioned quality of fluidity cannot be demanded to the same extent from copying inks as from writing inks. Copying inks are more thickly-fluid, and possess also the property—which is not desirable in ordinary writing—of remaining wet for some time.

3. Durability.—A good ink should be durable, *i. e.*, it should for a long time retain its color unaltered, and suffer but little, even if the paper written with it becomes moist or even wet; however, but few inks possess this property.

The quality of durability also includes the inalterability of the ink in the air. Good ink should on exposure to the air gradually dry to a lustrous mass, and even when much diluted should not mould. It is not difficult to fullfil this condition, since on account of their composition some inks have a poisonous effect on moulds, thereby preventing their development; whilst others, though subject to rapid decomposition, can be readily protected by the addition of certain antiseptic substances.

4. Inalterability.—For certain purposes—especially for writing important historical documents or other records—it is desirable that the ink used should not only be capable of resisting the ravages of time and accidental attacks (as the paper becoming moist or mouldy), but also intentional attacks by means of chemical agents. It may be plainly stated that it is impossible to entirely fullfil such demand, because it would require the discovery of an organic combination capable of resisting all agents, and at present such a combination is not known, nor is it likely to be known.

While ordinary writing inks cannot resist the action of chemical agents, certain other inks—namely, those prepared with the assistance of carbon—possess great powers of resistance, and of all masses used for the execution of written characters, printing alone is absolutely unassailable. It can only be destroyed simultaneously with the parchment, paper, etc., upon which it is used. But, unfortunately, printing ink can scarcely be prepared in a state suitable for writing with the pen. Besides carbon, certain dark-colored combinations of organic origin—the so-called humin bodies—possess great power of resisting chemical agents, without, however, being absolutely resistant, as is the case with carbon.

Intensity of color, fluidity, and a certain degree of durability are, therefore, the properties which may be demanded from every good ink, and in the manufacture of ink it must be sought to effect the presence of all these properties without neglecting one or the other.

Writing inks might be classified according to the color of the ink or the principal chemical combinations contained in it. Violet ink, carmine (red) ink, etc., are terms which would correspond to the first mode of classification, and gallic acid ink, madder ink, chrome ink, hematoxylin ink, etc., to the latter.

However, it may here be remarked that, generally speaking, the names given to the various inks, are nothing but names, and, as an example, it may be stated that in the fabrication of many inks which are sold as madder or alizarin inks, neither madder nor alizarin (a substance contained in madder) are used.

• It is not intended to adhere to a strict classification, there being no special advantage in doing so, but the inks belonging together according to their color will be described in a succession which is dependent partially on the mode of preparation and partially on the similarity of materials used.

Since black writing ink is the most important, its preparation will be discussed first.

## Black Writing Inks.

Chemically black writing inks differ essentially from each other, and they may be arranged into groups, namely, those which contain a *tannin combination* and those which are free from it. The inks containing tannic acid may, according to the raw material which yields the tannin, be again divided into gallotannic acid inks, catechu tannic acid inks, etc. The inks free from tannic acid, or those which, besides tannin, contain other substances, may be divided into chrome inks, alizarin inks, logwood inks, etc. It may, however, be remarked, that this division is not absolutely correct, since the dye-wood extracts used in the manufacture of ink may also contain certain quantitics of tannin.

~ The black writing inks, which are of the greatest importance and have been known for the longest time, are those which contain a tannin combination. Though their manufacture is the least expensive, they cannot be especially recommended, since, as a rule, they lack that

degree of durability expected at the present time of good inks. Inks containing tannin may even be called antiquated, and no doubt will soon entirely disappear from commerce:

Inks containing tannin .- These inks contain almost without exception a body of the tannic acid group in combination with ferric oxide. Tannin-like bodies being widely diffused throughout nature, it will be seen that a large number of vegetable raw materials may be employed for the manufacture of ink. Although the tannic acids occurring in the various vegetable substances closely resemble each other in a chemical respect, they are nevertheless plainly distinguished by certain prop-. erties, and the inks prepared from them also show different properties. While some tannic acids yield with ferric oxide bluish combinations and corresponding inks, others yield combinations of a peculiar greenish color, which changes only after sometime to a deep black. The properties of an ink correspond to those of the tannin contained in it. Some inks yield a bluish, others a greenish writing, which turns black only after sometime. Tannic acid inks which appear entirely black when flowing from the pen are generally already so far changed that they no longer penetrate into the paper and yield a writing which cannot lay claim to durability.

As regards the materials which yield tannin, the bodies prescribed in the various directions for preparing ink may be enumerated as follows :—

Nut-galls, valonia, oak bark, the barks of the sumach, willow and poplar, elm-wood, the bark and wood of the horse-chestnut, the sloe, berries of the buck-thorn, etc. This enumeration, however, is by no means complete, and it may be briefly stated, that every vegetable substance—be it bark, wood, fruit, leaf, or excrescences as long as it contains tannin may be used for the preparation of ink.

Before entering upon the discussion of the properties of the materials yielding tannin, it is considered necessary to explain the principal chemical properties of the most important tannic acids, since only with a thorough knowledge of them is it possible to understand the processes taking place in the formation of ink. By tannic acids are here understood certain chemical combinations contained in nut-galls, valonia, the barks of trees, etc., and which can be separated from them in a pure state.

Tannic acids.-In all the higher plants occur combinations which, with the so-called basic bodies, may form salts. Such compounds are called acids and are soluble Many of them are distinguished by a characin water. teristic astringent taste and are known by the collective term of tannic acids or tannins. By bringing a tannin solution together with a glue solution, the tannin forms with the glue an insoluble combination, and by carefully adding tannin to a fluid containing glue, all glue, and vice versa, all tannin, may be separated from it in the form of flaky masses, which, to a certain extent, consist of tannate of glue. The tannins also combine with animal skin, which thereby acquires the property of resisting putrefaction. For this reason tannic acids or the materials in which they occur are largely employed in the preparation of leather, in dyeing, printing, etc.

Besides the above-mentioned properties all tannins possess the common property of forming, when brought together with iron salts, either blue-black or greenish fluids. Furthermore, their solutions readily change, the consequence of such alteration being that the colors of the inks are frequently changed and that inks containing tannin may be readily destroyed by the formation of mould.

Gallotannic acid or tannin occurs in large quantity in nut-galls, especially in the Chinese variety, and exists also in sumach (*Rhus coriaria*), in tea and many other plants. It is readily soluble in water, spirit of wine, ether, etc., and also in mixtures of these bodies. To obtain it in a pure state, it is, however,

best to use only ether as a solvent.

To prepare gallotannic acid finely pulverized nut-galls are exhausted with ether in a percolator (Fig. 1). The latter is arranged as follows: It consists of a glass funnel, T, narrowing towards the top and provided with a neck, which is closed by a well-fitting The funnel is placed by stopper. means of a cork upon the flask, F. Two small glass tubes connected by a rubber tube are inserted in the stoppers of the flask and the funnel and permit the fluid contained in the funnel to sink down, and the air contained in the flask to enter the funnel. By this



arrangement volatilization of the ether is rendered impossible.

The operation begins by plugging the point of the funnel with cotton, the purpose of this being to prevent

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the powdered nut-galls from falling through, and the fluid from running off too rapidly. The funnel is then nearly filled with powdered nut-galls, and after pouring ether over them, the apparatus is closed and allowed to stand until no more liquid drips off.

The liquid, which after sometime collects in the flask below, consists of two distinct strata: the lower is a very strong solution of almost pure tannic acid in water; the upper consists chiefly of ether.

The ether is poured off and the solution brought into a shallow dish, which is covered with blotting-paper and allowed to stand until the fluid evaporates and a slightly yellowish powder remains in the dish. This powder is pure tannin, to which, however, some water still adheres. To free it from the latter the dish, together with a vessel filled half-full of strong sulphuric acid, is placed under a glass bell for several days. The sulphuric acid absorbs the water and the gallotannic acid is in this manner obtained as an almost pure white powder without the slightest tendency to crystallization and of an exceedingly astringent taste.

By exposing an aqueous solution of tannin to the air, an abundant vegetation of mould soon forms on the surface, and by a special process of fermentation the tannin thereby undergoes a peculiar change, in consequence of which it is converted into a new acid, the socalled *gallic acid*. Dry gallotannic acid, when heated by itself, is partially carbonized and partially converted into a new volatile body, the so-called pyrogallic acid or pyrogallol.

Gallic acid.—This acid occurs in divi-divi (the fruit of *Cisalpina coriariu*), in tea, in pomegranate root, and in many other plants. Nut-galls also contain very small quantities of it. It may be prepared by treating the vegetable substances containing it with hot water and allowing the solution to cool. The brownish crystals which separate are freed from the coloring matter by recrystallization, with the addition of pulverized animal charcoal.

It is, however, most advantageously prepared from nut-galls. By moistening coarsely-powdered nut-galls with water the entire mass will, in a short time, be covered with a very luxurious growth of mould, and in consequence of a peculiar process of fermentation gallic acid is formed from the gallotannic acid. The gallic acid thus produced may by recrystallization be obtained in a pure state.

Gallic acid differs essentially from gallotannic acid in that it leaves solutions of glue and albumen unchanged. By bringing it together with ferric salts a *deep-blue* fluid is obtained. It is especially the latter property on which the value of gallic acid for the preparation of ink depends.

Pyrogallic acid or pyrogallol.—This body is formed when gallic acid is heated to between 410° and 419° F. It crystallizes in shining white needles, and is readily soluble in water. It reduces the salts of silver, gold, etc., to the metallic state, and colors ferrous oxide solutions blue-black.

Catechutannic acid is contained in "catechu," a brown extract which is prepared in India from several plants, viz., Areca Catechu, Acacia (Mimosa) Catechu, and Nauclea Gambir. To prepare the acid in a pure state boil the catechu with water and compound the decoction with sulphuric acid. A precipitate is formed which consists of a combination of catechutannic acid with sulphuric acid. By dissolving this combination in boiling water with the addition of carbonate of lead, a precipitate of sulphate of lead is formed, while pure catechutannic acid passes into solution. Catechutannic acid may be obtained in a more simple manner by extracting catechu with ether.

Chemically pure catechutannic acid bears a close resemblance to gallotannic acid, but may be distinguished from it by the coloration it produces with iron salts, it yielding with the latter a peculiar *dirty-green* precipitate.

Kinotannic acid forms the principal constituent of "Kino," a reddish-brown extract, which is prepared from the juice of *Pterocarpus erinaceus* and *Coccoloba uvifera*. With ferric salts it gives a *blackish-green* precipitate.

By processes of fermentation which resemble those by which gallotannic acid is converted into gallic acid, kinotannic acid is changed to kino-red.

Morintannic acid or maclurin is the coloring matter of "fustic" or the wood of Morus tinctoria, and separates from a hot aqueous solution as a yellow crystalline powder. It has an astringent taste and with ferrous salts yields a *blackish-green* precipitate.

By heating morintannic acid it yields a new acid, *pyro-morin acid*, which stands in the same relation to morintannic acid as pyrogallic acid to gallic acid.

The above-described tannins are of special importance to us on account of their behavior towards soluble iron salts. To be strictly accurate, a distinction should be made between *ferrous* and *ferric* salts, since there is a difference in the color produced with these salts by means of a tannin. However, in practice this difference is of small importance, the ferrous salts possessing the property of being converted into ferric salts when brought in contact with the air, and ink prepared for sometime will always contain certain quantities of the latter salts. Furthermore, this conversion of the ferrous into ferric salts is sure to take place when the characters written with the ink upon the paper dry and the writing has for sometime been exposed to the air.

The colorations which the various tannins yield with iron salts (ferrous as well as ferric salts) may be grouped as follows:—

Gallotannic acid with ferric salts : black-blue.

Gallic acid with ferric salts : dark-blue.

Pyrogallic acid with ferrous salts : black-blue.

Catechutannic acid with ferrous and ferric salts: dirty-green.

Kinotaunic acid with ferric salts : black-green.

Morintannic acid with ferric salts : dark-green.

The above statement sufficiently indicates the color an ink will show with the use of one or the other material. To obtain a *deep-black* ink it will be necessary to choose one of the tannins occurring in nut-galls.

Since in practice it is impossible to work with the pure acids, they being too expensive, inks with entirely pure tones of the indicated colors will never be obtained. The color will always incline towards a brownish or blackish shade, since the extracts from the raw materials contain substances which exert an influence upon the color of the ink. For the practice this is, however, of small importance, the principal object being to pro-

duce an ink which will yield deep-dark and durable writing.

The raw materials which yield the tannin necessary for the preparation of ink occur in commerce in very varying qualities. It will, therefore, be necessary to give a somewhat detailed description of the more important ones, so that the manufacturer in buying them may be able to distinguish the good from the bad.

Ferric salts being absolutely necessary for the preparation of inks containing tannin, the properties and mode of preparation of these salts will also be described, so that in case of need, the manufacturer may prepare them himself.

## IV.

## THE RAW MATERIALS USED IN THE PREPARA-TION OF INKS CONTAINING TANNIN.

Nut-galls.—Nut-galls are morbid excressences formed on the leaves and leaf-stalks of various species of oaks by the sting of the gall-insect. The quality of the nutgalls as an article of commerce being chiefly of interest to the manufacturer of ink, it is not necessary to enter into details regarding their formation. However, it may be briefly stated that the nut-gall forms over the egg of the gall-insect and that the latter generally passes through its entire development in the nut-gall and escapes as a perfect insect through a perforation which it produces by biting. Nut-galls showing no

perforation and, hence, still containing the insect, also occur in commerce.

Commercially two varieties of nut-galls are especially distinguished, viz., *light* and *dark*. There are, however, further subdivisions into white, yellow, green, blue and black nut-galls. Those without perforation—hence, still containing the insect—are justly considered the best, it having been shown that they contain more tannin than those from which the insect has escaped.

Black nnt-galls, of a good quality, contain up to 27 per cent. of tannin, and altogether about 35 to 37 per cent. of soluble extractive substances. The nnt-galls are of almost a spherical form, and of the size of a pea up to a small nut. A good nut-gall must be heavy, and when cut through show a compact mass. If it shows little weight, and the interior is filled with a powdery or friable mass, the article is of little value, the content of tannin being very small. Many examinations have shown that nut-galls derived from southern countries are richer in tannin than those from more northern regions.

Aleppo nut-galls, also called Levantine nut-galls, are considered the best; next come Morea nut-galls, Smyrna nut-galls, Marmora nut-galls, and Istria nut-galls.

Good qualities of nut-galls are also brought from France, Hungary and Italy, as well as from Senegal and Barbary.

The characteristics of a good nut-gall, as generally accepted by merchants, are, an almost spherical form, a size not exceeding that of a cherry, prickly surface, without perforation, and a considerable weight.

The so-called Chinese nut-galls have a smooth outer

shell, which frequently shows a somewhat reddish color, and can be readily removed. After removing the outer shell, a brown pulp containing many dead larvæ of insects appears. It is not possitively known from which plant these nut-galls are derived, nor are the gallinsects known which produce them.

Another kind of nut-gall is produced by the sting of a gall-insect in the cups of young acorns. They appear in the form of shapeless, angular, dense masses of a brown color, which sit in the cups instead of acorns. They are collected in August, Hungary being the chief place of production in Europe, though a considerable quantity is also gathered in the oak forests of Asia Minor.

The chemical constitution of these two varieties of nut-galls is the same, both being distinguished by a large content of tannin and extractive substances; and they are, therefore, much used in the preparation of leather and ink, and in dyeing, printing, etc.

*Tan.*—This is the bark of the oak, elm, poplar, willow, and some other trees, bruised and broken by a mill, and, as is well known, used for tanning hides.

Tanners spread out the tan once used in layers about 5 inches high, and dry it, in order to re-employ it later on in the preparation of leather. From the drying tan an odor, which is anything but agreeable, is evolved, the origin of which is due to various processes of fermentation not yet accurately understood.

However, by these processes of fermentation the *gallotannic* acid originally contained in the tan is converted into *gallic* acid. All tanners agree that for the preparation of leather gallotannic acid is far better suited

than gallic acid, the latter, it is claimed, rendering the leather brittle. Hence, tan once used is of but little value to the tanner.

However, for the manufacture of ink, gallotannic acid and gallic acid possess nearly the same value; and for this reason, tan once used for tanning, and dried, may be suitably employed in the preparation of ink, especially as it can generally be had at a very low price.

Nut-gall extract or tannic extract occurs in commerce in the form of shining black-brown masses of an exceedingly astringent taste. It is prepared by extracting nut-galls, fresh tan and other materials rich in tannin with water and carefully evaporating the liquid to the consistency of syrup. In cooling it congeals to a solid, brittle substance.

Properly prepared nut-gall extract should chiefly consist of tannin, and must completely dissolve in water without a carbonaceous residue. It should have an exceedingly astringent taste. When the price demanded for the extract is not too high, it forms an excellent material for the preparation of ink, especially for manufacturers, who, for want of room, cannot kcep on hand a considerable stock of nut-galls, etc. The process of preparing ink with this extract is also very simple.

Attention must be called to the fact that nut-gall extract is liable to the formation of mould when exposed to moist air, and should, therefore, be stored in a dry room. Barrels or boxes lined with paper and provided with well-fitting lids may be recommended for the purpose.

Catechu.—This is an extract prepared principally from the wood of Acacia (Mimosa) Catechu. The wood, which is heavy and very durable, is covered by a dark brown fibrous bark, and consists of the whitish alburnum, and of the dark-colored heart-wood, varying in color from red-brown to blackish-brown. The latter portion is cut into chips, which are boiled with water in earthen pots arranged over a rude fireplace, the decoction when sufficiently strong being decanted or strained into other vessels, in which the evaporation is continued until the extract is of sufficient consistency to be poured into chay moulds, into cups formed of leaves, or upon mats covered with the ashes of cow-dung.

Catechu is chiefly exported from Pegu and Calcutta. Two varieties are mostly found in commerce: *yellow* and *brown* catechu.

The *yellow* catechu occurs in the form of cubes the size of a walnut; which, when treated with boiling water, color the latter yellow and impart to it a disagreeable, sweetish, astringent taste. For the manufacture of ink and for dyeing the yellow catechu is the more valuable product.

The *brown* catechu is denser and heavier than the yellow variety, and forms shining dark brown masses of a sticky consistency, which yield a red-brown decoction.

Catechu contains catechutannic acid and varying quantities of another acid to which the term japonic acid has been applied. The brown catechu contains a considerably larger quantity of the latter than the yellow. Since catechutannic acid is the only important body for our purposes, it is evident that the brown catechu is not desirable for the preparation of ink, and should not be

#### INKS CONTAINING TANNIN.

bought by the manufacturer. According to an examination of the two varieties of catechn they contain :---

	Yellow catechu.	Brown catechu.
Tannin	54.5 per cent.	48.5 per cent.
Extractive substances	34.0 ''	36.5 "
Vegetable mucus .	6.5 "	8.0 "
Insoluble constituents	5.0 "	7.0 "'

Purified catechu containing no constituents insoluble in water is occasionally found in commerce. It is still more valuable than yellow catechu. The great demand for this product led to the manufacture of a spurious article, which was brought into commerce under the name of catechu extract or *cachou épurée*. It consisted of brown catechu mixed with about  $\frac{4}{10}$  and even more of bullock's blood.

*Kino.*—Under this name is brought into commerce a brown-red, brittle mass, which, with alcohol or water, forms a beautiful red-brown solution, and contains, bc-sides the characteristic kinotannic acid, other vegetable extractive substances. Several different varieties of kino occur in commerce, the following being the principal ones :—

African kino, from Drepanocarpus Senegalensis; East Indian kino, from Nauclea Gambir.

Jamaica, West Indian or Caracas kino, from Coccoloba uvifera, L., or sea-side grape.

Australian or Botany Bay kino, from Eucalyptus resinifera.

The best variety of those mentioned above is the African or Gambia kino. It is, however, very seldom found in commerce in an unadulterated state. Fustic.—The wood of the Morus tinctoria, a tree growing in the West Indies, contains morintannic acid or maclurin. The species of sumach, *Rhus coriaria* and *Rhus cotinus*, very likely contain the same, or at least very similar dye-stuffs. Fustic is used for dyeing yellow, and also, together with iron salts, for dyeing black, and in the manufacture of ink, it yielding dark blackgreen ink.

As will be seen from what has been said in the preceding pages, the preparation of inks containing tannin actually depends on the fact that the various tannins yield, with iron salts, more or less dark green or dark blue, or even dark fluids, though the color of these fluids is not pure.

The great expense connected with the separation of the tannins in a pure state from the raw materials has, up to the present time, prevented the manufacture of ink in this manner, and, hence, no final result as to the correct proportions between tannin and iron combination has as yet been arrived at.

Iron combinations.—The iron salt most frequently found in commerce is the *ferrous sulphate*, commonly called *green vitriol*, *iron vitriol*, or *copperas*. To prevent mistakes it may here be remarked that there is an essential difference between *ferrous* and *ferric oxides*. Both, to be sure, consist of a combination of iron with oxygen, but in different proportions, the ferric oxide containing more oxygen than the ferrous oxide. However, it has a great inclination to absorb from the air sufficient oxygen to be converted into ferric oxide. In consequence ferrous salts are not durable, and when for sometime exposed to the air are gradually converted into ferrous salts. Ferrous salts are sea-green, while ferric salts are brown-red. Green bottle-glass contains ferrous oxide, but brown bottle-glass ferric oxide.

Ferrous sulphate or green vitriol is found in commerce in large crystals, which have a very disagreeable, metallie and astringent taste, dissolve readily in water, and, when for sometime exposed to the air, become coated with a rust-brown powder of basic ferrie sulphate. Ferrous sulphate being obtained in large quantities as a by-product in several chemical processes, its price is so low that it would not pay for the ink manufacturer to prepare it himself.

However, as it may be desirable for experimental purposes to prepare this salt in a pure state—and especially entirely free from ferrie oxide combinations—the process will here be briefly described.

To prepare entirely pure ferrous sulphate, pour over iron—old nails, barrel hoops, etc.—dilute sulphuric acid. The fluid becomes heated to a considerable extent and evolves, with violent foaming, a large quantity of hydrogen gas. When this evolution has ccased, filter the hot solution into a vessel containing a quantity of strong spirit of wine equal to that of the iron solution.

As soon as the iron solution comes in contact with the spirit of wine, a delicate pale-green powder, consisting of pure ferrous sulphate, is precipitated. The crystalline powder is dried between blotting-paper, and kept in a bottle hermetically closed by a stopper.

Inks prepared with the assistance of ferrous sulphate after standing for sometime contain, besides ferrous tannate, also ferric tannate, which has been formed by the ferrous oxide absorbing oxygen from the air. It may here be remarked that inks prepared according to antiquated directions, by dissolving iron in strong vinegar and adding decoction of nut-galls, contain ferrous oxide in the form of ferrous acetate.

Ferric sulphate.—This salt is prepared by adding to a solution of ferrous sulphate some nitric acid and heating the fluid to boiling. Since the ferric oxide requires for its solution more sulphuric acid than the ferrous oxide, it may happen, especially if but a small quantity of nitric acid has been used, that a rust-colored precipitate, consisting of basic ferric sulphate, is formed. The fluid is then either filtered from the precipitate or it is carefully mixed with a small quantity of sulphuric acid, which by heating redissolves the precipitate. An excess of nitric acid should be carefully avoided, otherwise the black fluid—the ink—formed by the addition of nutgall extract would in a short time be discolored.

It may here again be mentioned that these pure materials, the preparation of which has just been described, serve only for experimental purposes, they being too expensive to be employed in the actual preparation of ink.

Finally, the execution of experiments may be highly recommended to every manufacturer, especially when he intends to work with new materials containing tannin whose behavior he does not know. In using ferrous sulphate, special care must be taken that the product is entirely free from nitric acid and does not contain an excess of sulphuric acid, since an acid fluid shows an entirely different behavior towards a liquid containing tannin than one free from an excess of acid.

# V.

# CHEMICAL CONSTITUTION OF INKS CONTAINING TANNIN.

INSTEAD of pure tannins the above-mentioned raw materials are always used in practice; however, they contain a larger number of compounds, which even combine with the ferrons or ferric oxide and influence the color and other properties of the ink.

According to experiments by the chemist Dr. Bostock, the following processes take place in mixing a decoction of nut-galls with freshly prepared solution of ferrous sulphate: The ferrous oxide combines—1, with the gallotannic acid; 2, with the gallic acid; 3, with the vegetable mucilage; and 4, with the extractive matter. For the purpose of preparing ink, only the combinations of the gallotannic and gallic acids with the iron are of importance, since they yield the dark-colored combinations which constitute the distinctive character of ink.

The combinations of ferrous oxide, mucilage, and extractive matter, however, deserve mention, since they frequently render the ink too thickly fluid and impart to it a great inclination to the formation of mould. It will also be found that an ink containing these substances rapidly becomes paler and yields a black sediment, the latter consisting chiefly of mucilage and extractive matter in combination with ferric oxide. By the deposition of these at first flocculent bodies, the very finely divided substance consisting of tannin and ferrous oxide, which imparts to the ink its characteristic color, is also precipitated, the ink thereby soon becoming paler.

Several experiments will prove the fact that only the tannins are the essential constitutents of the decoction of nut-gall, if, for instance, an extract of nut-galls prepared cold is heated to boiling and for sometime kept at this temperature. On cooling a flocculent precipitate, consisting of the extractive matter insoluble at the boiling temperature, is separated.

Now if this precipitate is removed by filtering and the clear liquid exposed to the air, it will in a few days be covered with a thick coating of mould. The latter does not only procure its sustenance from the dissolved substances, but also effects considerable chemical changes in the fluid, the gallotannic acid being completely converted into gallic acid, while the extractive matter is at the same time almost entirely destroyed. If the mould vcgetation is for several weeks allowed to remain upon the fluid, the latter contains but few foreign substances and may be considered a quite pure solution of gallic acid in water.

By boiling the fluid filtered off from the mass of mould, in order to kill any mould-germs still present, and then adding green vitriol solution, an ink of a beautiful blue-black color is immediately obtained, upon which no mould will form even if it be allowed to stand for weeks in an open vessel. This ink has, however, the defect of becoming paler after standing for sometime, and forming a black sediment, the cause of this being that the density of the fluid is too slight to keep the heavy precipitate of iron and gallic acid in suspension.

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Experiments have shown that the bodics which cause the black coloration of the ink—the ferrous and ferric tannates and gallates—are solid bodies which in a finely divided state are suspended in the colorless fluid, and are not present in solution, as is frequently erroneously supposed. Hence, it follows that the fluid must possess sufficient density to keep the precipitate in suspension. In case the fluid does not possess this property, it must be imparted to it by the addition of an indifferent body which dissolves in it. To such bodies the term *inspis*sating agents is applied.

As inspissating agents, gum-arabic or dextrin are used; sugar, which is occasionally employed, is less suitable. Dextrin being the cheaper material, its use would be more preferable than that of gum-arabic, but it has the disagreeable property of absorbing water from the air, whereby the writing for sometime remains sticky. The use of sugar as an inspissating agent is unsuitable, partially on account of its comparatively high price and, partially because it readily undergoes mucous fermentation in the ink, whereby the latter is changed into a thick mass, drawing threads, and is thus absolutely unfit for writing.

When using ink prepared with green vitriol (ferrous sulphatc), it will be observed that the writing first shows a bluish or greenish color, which after a few hours becomes deep black. This is due to a chemical change taking place in the ink, which consists in the conversion of the ferrous oxide by the absorption of oxygen from the air into ferric oxide, the combinations of the latter with tannin possessing a darker color than those of the former. By substituting ferric sulphate for the ferrons salt an ink is obtained which immediately yields lustrous, perfectly black writing.

With the varying content of tannin in the different raw materials it is impossible to determine beforehand the quantity of iron salt which must be used for a determined quantity of nut-galls, etc., in order to form ink. Hence, in the various directions for preparing ferro-gallic inks, the statements regarding the quantity of green vitriol to be used differ very much, some prescribing double and three times the quantity of others. In our opinion the quantity of green vitriol prescribed in most directions is too high, and the yellowing of the ink, as is frequently observed in old documents, is due to an excess of iron salts, which acts upon the black combination of tannin with ferric oxide, gradually destroying it, so that finally nothing remains but an insoluble combination (basic salt) of ferric oxide and sulphuric acid, which shows the yellowish-brown color of old writings, or of repeatedly washed ink-stains in linen.

Experiments made regarding the proportion between nut-galls and green vitriol have shown, that an ink prepared by adding to the nut-gall extract a quantity of green vitriol equal in weight to that of the nut-galls, yielded very beautiful black writing, which, however, soon turned into brownish and finally into rust-color.

By increasing the quantity of green vitriol a black ink is still obtained, which, however, possesses less durability. The cause of this phenomenon is readily explained. By using a large quantity of green vitriol a certain quantity of it remains entirely unchanged, it being simply dissolved in the fluid. Now, in writing, the ink is spread in a very thin layer upon the paper and the green vitriol undergoes the same change as when exposed for sometime to the air: the ferrous sulphate is converted into basic ferric sulphate, which shows a rust-brown color.

When writing with green vitriol solution alone the characters are at first scarcely visible, the color of the solution being very pale green. However, the writing after sometime acquires the rust-color frequently seen in old, faded documents.

By constantly taking less green vitriol in proportion to the quantity of nut-galls the quantity of the former can be gradually much decreased, and the ink obtained will still show a good deep-black color. It would seem that in consequence of its finely divided state a comparatively small quantity of the precipitate, consisting of tannin and ferric oxide, suffices to impart to the ink its dark coloration.

By writing with a decoction of nut-galls alone upon paper, characters are obtained which at first are scarcely visible, but after some time become brownish, so that the writing is quite legible. Only in a special case, which will shortly be mentioned, the writing may entirely disappear.

The tannin combinations possess the property of being gradually converted in the air into dark-colored bodics, which also occur in wood mould and in good soil. The term *humin substances* is applied to these bodics. The conversion is, however, extraordinarily accelerated by the presence of alkaline bodics.

Now, paper as a rule contains small quantitics of lime, which are sufficient to accelerate the formation of humin substances and to effect the appearance of brown-colored writing. By passing a sponge moistened with sodasolution over writing executed with decoetion of nutgalls upon writing-paper, the characters appear very rapidly in a brown color.

If, however, the paper contains *free chlorine*, the writing will *not* be developed, and every kind of ink—even the very best—will in a short time be discolored, since chlorine rapidly destroys every organic dye-stuff, even indigo. It may here be remarked that great negligence has been shown in the manufacture of such paper, and that it possesses no durability. As previously mentioned, almost all modern papers contain lime or traces of chlorine; the presence of the latter always endangering the stability of the writing and of the paper.

There can be no doubt as to which ink is to be preferred, whether that containing green vitriol in excess or that in which tannin predominates. The first becomes yellow-brown and difficult to read, while the latter remains black and will in the course of time at the utmost lose its pure blue-black color and assume a brownish tone.

Inks with a small content of green vitriol always contain a certain amount of non-combined organic substance, which is readily decomposed and especially subject to a luxurious growth of mould, the latter forming even upon the writing, if the paper upon which it is executed is kept in a moist place, and causing the writing to fade.

However, the progress in chemistry has fortunately made known to us many substances, small quantities of which suffice to check the development of organisms in

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a fluid, and it is only necessary to add a small quantity of one of these substances to the ink in order to prevent the formation of mould or fermentation. The agent most frequently used for the purpose is carbolic acid. In a pure state it forms long, colorless needles, which readily dissolve in water. Less than 10,000 part by weight of the fluid of carbolic acid suffices to preserve even the most readily decomposable liquid. However, since by standing in the air the acid slightly volatilizes, somewhat more than the above-mentioned quantity is generally added to the ink, but care should be taken not to use too much, otherwise the odor would be perceptible. The carbolic acid may even contribute somewhat to the coloration of inks containing iron, it producing with ferric sulphate a violet color.

Besides carbolic acid, there are other substances—for instance, salicylic acid, borax, etc.—which prevent the formation of mould. These bodies, being odorless, are of importance for the preservation of food or perfumery, but not for the preparation of ink.

Although inks containing tannin are most readily decomposed, it is recommended to add a small quantity of carbolic acid also to other inks, with the exception of aniline inks, the dye-stuffs contained in them preventing the formation of mould without further assistance.

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## VI.

## DIRECTIONS FOR THE PREPARATION OF INKS CONTAINING TANNIN.

In the following a number of selected receipts for the preparation of inks containing tannin are given :---

#### A. Pure Tannin and Iron Inks.

Brande's nut-gall ink.\*—Aleppo nut-galls 3, crystallized ferrous sulphate 2, gum-arabic 2, water 60.

The ink is prepared in the cold way (without boiling), by bringing the finely-bruised nut-galls into a vessel (a bottle or wooden vat), pouring half the prescribed quantity of water over them, and dissolving in the other half, the ferrous sulphate and gum-arabic. On pouring the latter solution into the vessel containing the nut-galls a black fluid is formed which can at once be used as ink. However, it acquires complete blackness only after standing, with frequent stirring, for about two months, which is very likely due to the conversion of the ferrous into ferric oxide. When the ink has acquired the desired color it is allowed to stand quietly for a few days to permit the coarser particles to settle. It is then filled in bottles. The residue may again be used for the preparation of ink by treating it in the same manner with ferrous sulphate 0.5, gum-arabic 0.5, water 15.

\* The figures in all the receipts indicate parts by weight, except when otherwise stated.

This mode of preparing ink is very convenient, it requiring only the use of a single vessel and no boiling. It has, however, defects which can be readily determined from what has been said regarding the chemical constitution of inks containing tannin.

Since the presence of the woody parts of the nut-galls in the ink may have a disturbing effect, it is advisable to tie the pulverized nut-galls in a linen bag and suspend the latter in the vessel. The soluble substances are thus rapidly extracted, while the insoluble matter remains in the bag.

Besides gallotannate and a small quantity of gallate of iron, Brande's ink contains all the other extractive matter which is dissolved from the pulverized nut-galls by remaining for a long time in contact with water. Hence it is subject to the formation of mould and to becoming viscous. The effect of the last-mentioned phenomenon is that the ink is converted into an oil-like mass, which draws threads and adheres in thick drops to the pen, so that writing with it becomes almost impossible.

Such ink cannot be restored by filtering, and in most cases it is thrown away. It may, however, be doctored by mixing it with  $\frac{1}{20}$  of its volume of strong nut-gall extract and boiling for a few minutes.

By making many experiments this ink has been improved so far as to answer quite all the demands made on a cheap ink. The mode of preparation is given below. The product is not an ink of the best quality, but on account of its cheapness, it is very suitable for ordinary writing.

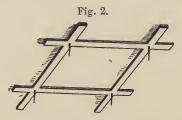
Brande's improved ink (according to Lehner).—Nutgalls 24 lbs., ferrous sulphate 16 lbs., gum-arabic 16 lbs., water 60 gallons, creosote 1 oz. Pour over the pulverized nut-galls in a barrel standing ugright sufficient water to cover them. In another vessel dissolve the ferrous sulphate and gum-arabic, mix the solution with the creosote and add the whole together with the remaining quantity of water to the nutgalls, stirring constantly. Then cover the barrel and stir the fluid once every day. In about three weeks the ink is sufficiently black and can be filled in glass bottles, a wooden ladle being used for the purpose.

The ink prepared in this manner keeps for years without decomposition, and a large quantity of it can be prepared at an extremely small cost.

Tannin ink according to Ure .- This ink, which is distinguished by an agreeable blackness and great durability, is prepared according to the following formula: Nutgalls 18, ferrous sulphate 8, gum-arabic 7, water 145. Bring the powdered nut-galls into a boiler, add 130 parts of water, and mark the level of the fluid on the wall of the boiler. Then heat to boiling, stirring constantly to prevent the powdered nut-galls from burning to the bottom of the boiler, and keep the fluid vigorously boiling for two hours, from time to time replacing the water lost by evaporation, by filling the boiler up to the above-mentioned mark. In order to obtain the cold fluid entirely clear it is passed through a cloth-filter (Fig. 2). Such a cloth-filter is very useful in the preparation of ink, and consists of a square wooden frame, the pieces of which are joined by long nails with the points upwards. A cloth is secured to these nails, and, if necessary, covered with blotting-paper. By the weight of the fluid poured upon it, the cloth sags down, and to

#### INKS CONTAINING TANNIN.

prevent its tearing, it is advisable to support it by cords diagonally fastened to the frame.



While the nut-gall extract is passing through the filter, the ferrous sulphate and gum-arabic are dissolved in 15 parts of water, and the solution is added to the filtered decoction. It is advisable to keep the ink in a barrel only partly filled, since by the action of the air it becomes blacker.

To preserve this ink, it may be mixed with a small quantity of carbolic acid or a few drops of oil of cloves, which also prevents the formation of mould. A few tablespoonfuls of ordinary coal tar poured into the barrel also suffice. Carbolic acid, however, is the best agent for the purpose.

English office ink.—Nut-galls 200, ferrous sulphate 50, gum-arabic 50, water 2400.

Divide the entire quantity of water in three portions: one of 1000 parts, another of 800 parts, and the third of 600 parts. Boil the nut-galls with the largest quantity of water for  $1\frac{1}{2}$  hours, and, after drawing off the decoction, repeat boiling with the second portion of water for one hour, and then with the third portion for half an hour. The first two decoctions are combined, while in the third the gum-arabic and ferrous sulphate are dissolved with constant stirring. Finally, all the fluids are mixed.

Boiling the nut-galls with several portions of water may be highly recommended, all soluble constituents being thereby completely dissolved.

Add to the ink a small quantity of tar and thoroughly stir it once a day for a week. Then allow it to stand quietly for several weeks, and, when entirely clear, fill it in bottles.

To recognize whether an ink is clear, *i. e.*, that nothing besides the ferrotannate is suspended in the fluid, bring a small quantity of the ink into a large tumbler and add sufficient water to render the fluid transparent. It should then appear bluish-black without a solid body being visible in it, and, after standing for sometime, form a very delicate black sediment, while the supernatant fluid only shows a slightly yellow-brown color.

American office ink.—Nut-galls 24, ferrous sulphate 5, gum-arabic 5, water 2000.

The peculiarity in the preparation of this ink is that the ferrous sulphate is previously subjected to roasting. For this purpose it is brought into an iron pan, or still better into an earthenware dish, and heated over an open fire. The ferrous sulphate thereby loses, first, its water of crystallization, and its green color is changed to white; after heating for sometime it acquires a yellow color, in consequence of the formation of ferric sulphate.

When prepared according to this process, the roasted ferrous sulphate contains ferric sulphate besides unaltered ferrous sulphate. However, with somewhat stronger heating, a portion of the ferrous sulphate is converted into basic ferric sulphate, which is insoluble, and, hence,

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does not assist in the formation of ink. The preparation of roasted ferrous sulphate has therefore been somewhat modified, the operation being conducted according to the following method, which yields very favorable results: Take ferrous sulphate 20, water 2, sulphuric acid 1; mix the sulphuric acid with the water, pour the mixture over the ferrous sulphate in a stoneware dish, and heat it slowly to the melting point of lead (599.4° F.). The roasted product thus obtained is completely soluble in water.

Care must be taken that the roasted mass does not contain an excess of sulphuric acid, otherwise the ink will possess the injurious property of strongly attacking steel-pens, a property which will render every kind of ink unfit for use.

Nut-gall ink according to Karmarsch.—Nut-galls 18, ferrons sulphate 7, gum-arabic 7, water 64.

Convert the solid substances into a coarse powder, pour 48 parts of water over them, and let the whole stand for one week, stirring once every day. Then add the remaining water, stir thoroughly, and the ink is ready for use.

This otherwise excellent ink being subject to the ready formation of mould, it is recommended to add a small quantity of carbolic acid, tar or a few cloves, the latter by their content of volatile oil also checking the formation of mould.

Nut-gall inks when not entirely free from acid possess the disagreeable property of strongly attacking steelpens. Hence to obtain these inks free from acid, bodies capable of neutralizing the acid are added. A formula for such an ink is as follows :— Link's steel-pen ink.—Nut-galls 112, ferrous sulphate 48, gum-arabic 40, water 1600, ammonia 1, spirit of wine 64.

The object of the ammonia (commercial water of ammonia) is to fix the free acid, and that of the spirit of wine to cover the smell of the ammonia and prevent fermentation. The addition of spirit of wine seems superfluous and even injurious, since, on the one hand, it increases expense, and, on the other, the ink, on account of the great volatility of the spirit of wine, must rapidly dry up in the air.

Link's improved steel-pen ink (according to Lehner).— On account of the importance of the subject this ink has been subjected to a thorough examination, and improved. Take nut-galls 112, ferrous sulphate 48, cupric sulphate (blue vitriol) 2, gum-arabic 40, water 1600.

To the finished ink add pulverized carbonate of ammonium so long as strong effervescence takes place. The object of the addition of cupric sulphate is to coat the pen with a thin film of metallic copper, which is less attacked by the ink than steel. By this means the surface of the pen is at least protected; however, this protection does not extend to the point of the pen, that being constantly ground off in writing.

# B. Inks Containing Gallic Acid.

The inks containing gallic acid combine with a beautiful blue-black color the valuable property of being far less subject to decomposition than the inks containing gallotannic acid. The preparation of these inks differs from that of the tannin inks in that it is endeavored to convert all the gallotannic acid into gallic acid. This conversion is effected by the formation of mould upon the nut-galls themselves, or upon the extract prepared from them, when allowed to stand in the air. However, as it may frequently be inconvenient to the manufacturer to have a vat with nut-gall extract stand for weeks, the operation may be simplified as follows :—

Fill a vat nearly full with the coarsely-powdered raw material containing the tannin (nut-galls, bark), pour in sufficient water of 68° to 77° F. to cover it, and put a lid upon the vat. In the moistened mass a luxurious growth of mould soon appears, which spreads out towards the top in the form of a gray-green cover, but in the interior has the appearance of whitish felt. In the course of eight to ten days all the gallotannic acid has been converted into gallic acid. To prevent further decomposition pour boiling water over the mass, whereby the mould is killed.

The solution of gallic acid collecting on the bottom of the vat is drawn off by means of a stop-cock, and used in the preparation of ink. The inks prepared with it possess, besides great stability, an agreeable blueblack color.

In the following, the most approved receipts for the preparation of inks containing gallic acid are given :----

Prime ink.—Nut-galls 5, ferrous sulphate 1, gumarabic 1, water 200, carbolic acid 0.02.

Pour the water over the powdered nut-galls, and let the whole stand until a vigorous formation of mould takes place. It may frequently happen, especially at a low temperature, that the formation of mould only commences after several days, and the conversion of the gallotannic acid into gallie acid progresses very slowly. To accelerate the process, scrape off the mould which has formed upon moist bread or leather, and add it to the mass. This forms an excellent nutriment for moulds, and the latter spread rapidly over and through the entire mass.

The mouldy fluid is filtered and mixed with the ferrous sulphate and gum-arabic. Finally the carbolic acid is added.

Runge's ink.—Nut-galls 8, water 64, ferrous sulphate 4, gum-arabic 2.

The bruised nut-galls are scalded with boiling water, and the mass is allowed to stand for two months. The fluid is then drawn off, the residue stirred up with some water, pressed out, and the fluid thus obtained combined with the first fluid. The ferrous sulphate is dissolved by itself in as little water as possible, while the gumarabic is dissolved in a portion of the gallie acid solution. Finally, all the fluids are combined.

Bolley's inks.—Dr. Bolley, formerly Professor at Zûrich, gives several directions for the preparation of inks, which are here inserted in order to show the difference of opinion amongst chemists regarding the preparation of ink :—

1. Nut-galls 125, ferrous sulphate 24, gum-arabic 24, water 1000.

This ink is quite good, but only a small portion of the tannin present is consumed in the formation of ink; a large portion remains unchanged.

2. Nut-galls 66, ferrous sulphate 22, gum-arabic 19, water 1000.

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This ink seems to contain exactly the sufficient quantity of ferrous sulphate.

3. Nut-galls 62, ferrous sulphate 31, gum-arabic 31, water 1000.

This formula contains a somewhat too large quantity of ferrous sulphate; at least writing executed with it fades sooner than that with the other inks.

Stark's iron ink.—Boil 12 ozs. of Aleppo nut-galls with  $4\frac{1}{2}$  quarts of water, dissolve in the decoction 4 to 6 ozs. of gum-arabic, and add to the cold fluid 8 ozs. of ferrous sulphate, 8 ozs. of indigo-carmine, and a few drops of earbolic acid.

This formula yields a beautiful ink, which is, however, somewhat expensive on account of the large quantity of indigo-carmine used.

Formulæ for cheap ferro-gallic inks.—I. Nut-galls 17 ozs., logwood 5 ozs., dextrin 7 ozs., alum 2 ozs., ferrous sulphate  $7\frac{1}{2}$  ozs., rain-water 5 quarts.

II. Nut-galls 20 ozs., dextrin 14 ozs., ferrous sulphate 14 ozs., rain-water 3 quarts.

III. Japanese nut-galls 63 ozs., dextrin 42 ozs., ferrous sulphate  $29\frac{1}{2}$  ozs., indigo-carmine  $31\frac{1}{2}$  ozs., water 25 quarts.

IV. (School ink.)—Japanese nut-galls 15 lbs., water 80 quarts, dextrin 6 lbs., ferrous sulphate 5, wood-vinegar 1, and mix with logwood extract 14 lbs., dextrin 12, water 100 quarts.

The cheapest iron ink.—Tanned leather contains large quantities of tannin, and waste of such leather can be advantageously utilized in the manufacture of ink and of glue. For this purpose pour sufficient water, to which has been added 1 pint of hydrochloric acid for every 100 quarts, over the waste in a vat to just cover it, and let the whole stand quietly for one week; then draw off the fluid, press out the swollen waste as much as possible, and treat it again in the same manner. The fluid thus obtained is filtered and mixed with sufficient ferrous sulphate to yield a deep-black ink. Before filling the ink in bottles it is allowed to stand in the air for several weeks, it acquiring thereby a greater depth of color.

The waste remaining in the vat yields, with proper treatment, a good quality of glue, and may be sold to a manufacturer of that article.

Blue-black ink.—Aleppo nut-galls "blue"  $4\frac{1}{2}$  ozs., cloves bruised  $\frac{1}{8}$  oz., cold water 40 ozs., ferrous sulphate (purified crystals)  $1\frac{1}{2}$  ozs., pure sulphuric acid 35 drops, sulphate of indigo  $\frac{1}{4}$  oz.

Macerate the nut-galls and cloves in the water during a fortnight; then press and strain through the clothfilter, add the ferrous sulphate previously powdered, dissolve, and add the acid and indigo solution. Shake or stir the mixture well; then set it aside for a week, and filter it.

The nut-galls should be free from insect perforations. The sulphate of indigo should be used in the form of a thinnish paste, neutral or nearly so.

Black ink for shading-pens.—Powdered nut-galls 18, ferrous sulphate 8, gum-arabic 7, water 145.

Boil the nut-galls in 130 parts of the water; then dissolve the ferrous sulphate and gum-arabic in the remaining 15 parts of water, and slowly add this solution to the former.

## VII.

#### LOGWOOD AND TANNIN INKS.

Logwood or Campeachy wood.—The logwood tree, Hæmatoxylon campechianum, is indigenous to the shores of the Gulf of Campeachy and to other parts of Central America, and has been introduced into and perfectly naturalized in Jamaica, St. Domingo, and other West Indian islands. It is 30 to 40 feet high, has many spreading and crooked branches, alternate leaves with four pairs of obcordate leaflets, small yellow flowers in lax racemes, and two-seeded legumes. The tree is felled when about 10 years old; the bark and light-colored sap-wood are removed, the red heart-wood alone entering commerce.

Logwood is met with in logs about 3 feet long, which consist of heart-wood, and from exposure are externally of a blackish-purple or red, internally of a brown-red color. By boiling logwood with water, the dye-stuff contained in it—the *hæmatoxylin*—passes into solution and imparts to the water a dark-red color. By compounding this decoction with dilute acids it acquires a crimson color, while in contact with iron salts it assumes a dark blue-black color.

Ammonia dissolves hæmatoxylin, the solution being rose-red, then purple, and finally blackish-red; the fixed alkalies produce similar solutions, and the color ultimately becomes yellowish-brown. The blackish ammonia solution contains hæmatein-ammonia, from which acetic acid separates *hæmatein*, which is soluble in alcohol and hot water, slightly so in ether, and forms a blackish-violet crystalline powder having a green metallic lustre. Hæmatein-ammonia causes, in a warm solution of a small amount of alum and with ferric chloride, deep-violet precipitates; with lead acetate, a brown one.

For the manufacturer of ink the use of ground logwood is very convenient, but unfortunately it is frequently adulterated with other substances and by moistening with water, so that it is not advisable to buy it in that state, except from a reliable firm.

Logwood extract.—For the manufacture of ink the use of logwood extract may be highly recommended, it offering many conveniences. Although it is relatively more expensive than logwood, it is cheaper in the end than the preparation of a decoction. It may be accepted as a rule that 12 to 15 parts by weight of the extract correspond to from 50 to 60 parts by weight of logwood.

Commercial extract of logwood forms either irregular pieces or thin disks with a shiny surface and of a dark black-brown color which readily dissolve in water. The residue remaining thereby, which should only constitute a very small quantity, consists of insoluble substances which are formed by the inevitable heating required in evaporating the extract.

Although decoction of logwood, as well as the solution of the extract, may yield inks by themselves—which will be referred to later on—they are preferably used as an addition in the manufacture of inks which otherwise would not show a sufficiently deep-black color.

Logwood inks are prepared by either simultaneously

boiling or macerating the logwood with the nut-galls, or by boiling the logwood by itself and combining the decoction with the nut-gall extract, or, finally, by dissolving the logwood extract with the assistance of heat in a very small quantity of water and mixing the solution with the other ingredients.

Logwood and tannin inks have the advantage of an agreeable black-blue color and of considerable fluidity; they also attack steel-pens less energetically than many pure tannin inks.

Logwood ink.—Nut-galls 9, ferrous sulphate 9, rasped logwood 9, gum-arabic 9, water 180, vinegar 180.

The nut-galls, ferrous sulphate, gum-arabic, and vinegar are brought together, the rasped logwood is boiled with the water, and the solution restored to 180 parts by the addition of water. It is then mixed with the other ingredients.

Logwood extract ink.—Nut-galls 36, ferrous sulphate 36, logwood 9, gum-arabic 36, water 300, vinegar 60.

This ink is prepared in exactly the same manner as the preceding. When finished it is once more strained through the cloth-filter.

Ribancourt's logwood ink.—Nut-galls 16, rasped logwood 8, ferrous sulphate 8, cupric sulphate (blue vitriol) 2, gum-arabic 6, sugar 2, water 200.

This ink is prepared by boiling the logwood with the water until one-half of the latter is evaporated. The hot solution is filtered, and after adding the other ingredients, stirred until solution is complete.

The ink, immediately after clarifying, which requires two or three days, is drawn off from the sediment and filled in bottles.

#### THE MANUFACTURE OF INK.

Various formulæ for logwood and tannin ink.—I. Digest 2 lbs. of bruised nut-galls in 2 quarts of alcohol at a temperature of 104 to 140° F. When about half the alcohol has evaporated add 3 quarts of water. Stir well and strain through a linen cloth. To clarify the solution, add glycerin 8 ozs., gum-arabic 8 ozs., and ferrous sulphate 1 lb. dissolved in water. Stir thoroughly from time to time for a few days, allow to settle, and put up in well-stoppered bottles for preservation. The addition of too much ferrous sulphate is to be avoided as causing the ink soon to turn yellow. Ink thus prepared is said to resist the action of light and air for at least 12 months without suffering any change of color.

II. Nut-galls 1 lb., gum-arabic 6 ozs., alum 2 ozs., ferrous sulphate 7 ozs., kino 3 ozs., logwood raspings 4 ozs., water 1 gallon. Macerate. This ink is said to write well on parchment.

## Logwood and Gallic Acid Inks.

As regards their general composition, these inks closely resemble the preceding, they only differing from them in that they contain no gallotannic acid, but only gallic acid.

Prime logwood and gallic acid ink.—Nut-galls 20, logwood 30, ferrous sulphate 20, gum-arabic 20, water 130.

This ink is prepared as follows :----

Pour 80 parts of water over the pulverized nut-galls in a capacious vat. An abundant formation of mould soon appears, and the gallotannic acid is converted into gallic acid, conversion being finished in about 14 days. The fluid is then drawn off from the powder, and the latter washed with sufficient water that the combined fluids amount to 100 parts.

The rasped logwood is boiled in 50 parts of water until the fluid is reduced to 30 parts, when it is drawn off while still hot. The ferrous sulphate and gum-arabic are then dissolved in the hot fluid and the whole is combined with the solution of gallic acid. In a few days a considerable sediment forms in the fluid. The supernatant liquid is an excellent pure black ink.

*Hæmatoxylin ink.*—Nut-galls 40, logwood 50, ferrous sulphate 30, gum-arabic 25, water 200.

According to the directions the pulverized nut-galls must remain in contact with water for at least three months, and the vessel containing them stand in a room having a uniformly warm temperature, so that the gallotannic acid be completely converted into gallic acid.

Comparative experiments, however, have shown that this conversion takes place in a much shorter time, fourteen days being sufficient for the purpose. The consequence of the action of the ferment for a longer time is the same as met with in other fermentations. The chemical process does not stop when the last particle of gallotannic acid has been converted into gallic acid, but continues on, so that ultimately a considerable quantity of the tannin originally present is changed to bodies which do not yield colored combinations suitable for the manufacture of ink. Furthermore, the continued action of the mould upon the nut-galls is a disadvantage, time and useful substance being lost, and, finally, it is of no importance to the ink manufacturer, whether the ink, besides gallic acid combinations, also contains gallotannic acid combinations or is entirely free from them.

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The mouldy nut-gall extract is boiled with the logwood for a few hours, the water lost by evaporation being constantly replaced. Finally, the ferrous sulphate and gum-arabic are dissolved in a small quantity of the decoction, and the solution is mixed with the other fluid.

## VIII.

#### FERRIC OXIDE INKS.

As previously mentioned, many inks acquire a deepblack color only sometime after their deposition upon the paper. This is due to the fact that the ferric oxide salts formed with tannins, possess a decidedly darker color than the respective ferrous oxide salts. For many years attempts have been made to bring into commerce ferric oxide inks which show a deep-black color immediately after their deposition upon the paper. For this purpose the ferrous sulphate is heated with the access of air in order to convert at least a portion of it into ferric oxide.

However, according to special experiments made in regard to this subject, it would appear that inks containing ferric salts exclusively possess no qualities of special value.

In the experiments above mentioned the ferric sulphate was prepared by boiling ferrous sulphate in solution with nitric acid, or by dissolving ferric hydrate in sulphuric acid.

By adding nut-gall decoction or gallic acid solution, formed by allowing the nut-gall decoction to mould, and either with or without the assistance of logwood extract, an ink was obtained which immediately yielded writing of a faultless black and a beautiful lustre.

After lying for sometime, the writing executed with this ink, however, lost its peculiar lustre, and finally, also, its intense black color, which passed into a brownishblack. Besides, all these inks possessed the defect of adhering but slightly to the paper, so that by the exercise of some care, the writing could be completely removed with the assistance of a soft sponge and water. Only writing a few years old withstood to a certain extent the action of water.

An explanation of this phenomenon may possibly be found in the fact that the ferrous combinations penetrate more deeply into the paper, and in the latter are gradually and only partially changed to ferric compounds. If this explanation is correct it will be readily understood that writing executed with ferrous oxide ink cannot be removed by simple mechanical washing, but only by chemical agents.

In regard to the change in color of inks containing only ferric oxide, it may be assumed that the browning of the writing is due to a portion of the ferric oxide separating from the combination.

Japanese ink.—This much-vaunted ink is a preparation which chiefly contains ferric tannate.

The ferrous sulphate is carefully roasted at not too high a temperature, and then mixed with gall-nut decoction and logwood extract. The ink is deep black, but possesses the above-mentioned defect of turning brown.

Like all ferric oxide inks, it is quite thickly-fluid. After writing with it the pen has to be carefully cleansed, otherwise the adhering ink dries to a tenacious crust, and the pen soon becomes useless.

Generally speaking, pure ferric oxide inks are of little value. On the other hand, inks which, besides ferric, also contain ferrous combinations, may be highly recommended on account of the beautiful black writing which they yield immediately after their deposition upon the paper.

To obtain such an ink, it is, however, not necessary to form special ferric combinations in it, they being formed by themselves when the ink is allowed for sometime to stand in the air, since the ferrous oxide possesses but little stability and constantly endeavors to change into ferric oxide.

## IX.

#### ALIZARIN INKS.

IN accordance with their name, these inks should contain alizarin. The latter is the red coloring matter of madder root (*Rubia tinctorum*); at present, however, almost all the alizarin used in dyeing is obtained by artificial processes. However, most of the inks found in commerce under the name of alizarin inks do not contain a trace of it nor any other constituent of madder. We do not know where this name originated; very likely it was arbitrarily chosen to deceive the public, and, if possible, also the chemist. Inks actually containing alizarin are distinguished by very excellent properties.

The inks previously described contain the combina-

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tions consisting of ferrous oxide and gallotannic acid or gallic acid in the form of very finely-divided solid bodies. By omitting the gum-arabic, which exclusively serves for the purpose of giving greater density to the fluids, and thus preventing the precipitate from sinking to the bottom, it will be found that the ink, when standing in a tall glass, will soon acquire a blue-black transparency and deposit a black precipitate.

This deposition of a precipitate can, however, be completely avoided by adding, when preparing the ink, an acid—acetic acid being especially suitable for the purpose. The precipitate dissolves in the acid.

Now, the so-called alizarin inks are nothing but inks made intentionally acid by acetic acid, or more seldom by sulphuric acid, and containing the ferrous tannate in a dissolved state.

The solution generally has quite a pale greenish or brownish color, but becomes intensely black in a few hours after its deposition upon the paper. The process taking place thereby is a twofold one: The solvent acetic acid—partially evaporates and leaves behind the dissolved body in a thin layer; another portion\_of the acetic acid is neutralized by the lime contained in the paper,\* but chiefly by the ammonia, which, though in very small quantities, is always present in the air.

By placing writing executed with alizarin ink, together with a small dish containing *aqua amononiæ*, under a glass bell, it turns almost immediately black.

It is evident that an ink containing free acid of such

\* The lime present in paper originates from the water used in the manufacture of the latter.

strength as acetic or sulphuric acid will strongly attack steel-pens. However, with a correct treatment of the pen, this is of little importance. By allowing, after writing once, the ink to dry upon the pen, a uniform, firmly-adhering coating is formed upon it, which protects the steel from any further action of the ink. Moreover, only a very small quantity of acid is required and every excess of it should be avoided. If the ink is too acid, the excess is neutralized by the careful addition of ammonia. Of the latter, not so much should, however, be added as to make the ink black, otherwise the latter does not contain everything in a dissolved form. But if too much has been added, the ink may be restored by mixing it with acid ink.

If neutralization of the acid is considered necessary, it is best to divide the ink into two portions and to saturate one portion with ammonia until it appears almost entirely neutral and then mix it with the other portion.

Alizarin inks being solutions, no sediment is formed in the bottles, even after standing for years, and since they possess great fluidity they are especially suitable for rapid writing, which has much contributed to their popularity.

A defect of the alizarin inks is their pale color immediately after their deposition upon the paper, the writing executed with some of them being at first so pale as to be scarcely visible, especially in an artificial light. This pale color may be overcome by adding to the ink an intensely colored dye-stuff, which later on, when the ink becomes black, is covered by it, but at first helps to make the writing plainly visible. Formerly indigocarmine was the chief agent used for this purpose, but since the invention of the much cheaper aniline colors soluble in water, the latter are frequently substituted for it. However, since indigo-carmine is a substance which renders good service as an addition to any kind of ink, and, furthermore, may be used in a pure state as a writing fluid and for stamping inks, a somewhat detailed description of its preparation is here given.

Indigo-carmine.—The beautiful blue dye-stuff indigo is the product of several species of plants of the genus Indigofera, growing in India and South America; also of Isatis tinctoria, Nerium tinctorium, Polygonum tinctorium, and other plants. It does not exist in these plants ready formed, but is obtained by macerating the plants with water, exposing the liquid in flat vessels to the air, and stirring up frequently. Fermentation soon sets in, and indigo is deposited as a blue powder. It comes into the market in the form of cubic cakes, which, when rubbed with a hard body, exhibit a copper-red lustre.

To prepare indigo-carmine, it is first necessary to produce indigo-sulphonic acid. Indigo dissolves completely only in fuming sulphuric acid (the so-called Nordhauseu sulphuric acid), and only if entirely free from moisture. The operation is as follows : Convert the indigo in a mortar to as fine a powder as possible. Then to remove every trace of moisture, carefully dry the powder in a capacious porcelain dish at a temperature not exceeding 248° F., and immediately pour fuming sulphuric acid over the warm dry powder. The quantity of sulphuric acid required is dependent on its strength and the purity of the indigo ; however, as a rule, for 1 part by weight of indigo (weighed dry) 4 of sulphuric acid are used. The sulphuric acid should be added very slowly, and under constant stirring with a glass rod. The mass thereby foams up, and hence the porcelain dish must be of sufficient capacity to prevent running over. When all the sulphuric acid has been added, stir thoroughly; then cover the dish, and allow it to stand 24 hours. In the course of this time the coloring substance of the indigo the indigotin—has combined with the sulphuric acid and formed indigo-monosulphonic acid or phænicinsulphuric acid. The latter might at once be converted into indigocarmine, but the resulting product would not possess the desired beauty, since by the action of the sulphuric acid certain constituents of the indigo are carbonized and the solution appears black instead of blue.

To free the liquid from these carbonized substances. dilute it with 10 to 12 times its quantity of pure water, pour the dilute solution into a large bottle and let it stand for a few days to allow the undissolved matter to settle. The clear solution, which in thin strata shows a beautiful indigo-blue, but in thicker strata a black color, is brought into a capacious porcelain dish and evaporated without boiling, being at the same time neutralized with potash (potassium carbonate). The latter, in a finely divided state, is added to the evaporated indigo-monosulphonic acid, carbonic acid escaping with strong effervescence and foaming. When the acid is neutralized, effervescence ceases and the fluid now contains potassium indigotindisulphonate or indigo-carmine in solution. From this solution the indigo-carmine may be obtained by careful evaporation; it is, however, generally preferred to separate it by salts.

Indigo-carmine, namely, has the property of readily

dissolving in water, but with difficulty in salt solutions. By now adding to the neutral solution an excess of potash or pulverized crystallized soda, the indigo-carmine separates as a doughy mass, which is collected upon a filter and washed with a very small quantity of water, and dried, whereby it frequently becomes coated with an efflorescence of sulphates or of soda (when no excess of sulphuric acid is present).

When dry, pure indigo-carmine represents a deep-blue mass with the characteristic copper-red lustre of indigo.

Indigo-carmine is readily soluble in water, a very small quantity of it imparting to the latter an intense blue color. In alcohol and salt solutions it is soluble with difficulty.

For the ink manufacturer it is not necessary to prepare the indigo-carmine in a solid form. For his purposes it suffices to concentrate to a certain degree the solution of indigo monosulphonic acid, completely neutralized with potassium carbonate, and preserve it in bottles. For the preparation of stamping inks or laundry blue it is, however, necessary to convert it into a doughy mass, which is effected by almost completely drying the residue remaining upon the filter, or, what is still better, by placing it upon thoroughly burnt bricks, which rapidly withdraw the water from it.

The efflorescence of sulphates upon the indigocarmine is a disagreeable phenomenon, it injuring the appearance of the article. It may be somewhat prevented by adding to the indigo-carmine a certain quantity of glycerin. The latter has the property of absorbing with avidity water from the air, and thus prevents the efflorescence of the salt, so that the indigo-carmine retains the nature of a dark-blue dough.

Office alizarin ink.—Nut-galls 100, ferrous sulphate 60, gum-arabic 10, vinegar 1000, indigo-carmine solution 200.

This beautiful green and very fluid ink is prepared by pouring the vinegar over the nut-galls, after a few days decanting off the tannin solution, dissolving the finely-pulverized ferrous sulphate and gum-arabic by boiling them in a portion of the fluid, mixing both fluids, and finally adding the indigo-carmine. Should the latter not be sufficient, add a larger quantity. It is best not to weigh the indigo-carmine, but keep a solution of it on hand and add 1 pint of it to 100 quarts of ink, stir vigorously and make a test. If the writing shows a beautiful blue-green color immediately after the ink flows from the pen, a sufficient quantity of indigo-carmine has been added. The finished ink is at once filled in bottles, and when shaken should represent a clear, dark-green fluid running down rapidly on the sides of the bottle.

Some ink manufacturers use a poor quality of beervinegar for the preparation of alizarin ink, in consequence of which the product becomes mouldy on exposure to the air.

To avoid this, and also to work more economically, it is recommended to use, instead of ordinary vinegar, crude wood-vinegar, which, in consequence of its mode of preparation from wood-tar, contains a very small quantity of carbolic acid. The latter gives to the vinegar an empyreumatic odor, but entirely prevents the formation of mould. Prime alizarin ink.—Nut-galls 40, iron solution 15, indigo-carmine 5, gum-arabic 10, wood-vinegar 10, water 100.

This ink surpasses all other alizarin inks in that it not in the least attacks steel-pens. The mode of preparing it, which is now published for the first time, is as follows: Treat the pulverized nut-galls with the water, to which 5 parts of the wood-vinegar have been added, for eight days, during which time the gallotannic acid is completely dissolved, but not converted into gallic acid, fermentation being suppressed by the presence of the wood-vinegar.

At the same time as the nut-gall extract, the iron solution is prepared. For this purpose bring any desired quantity of old wrought-iron into a barrel provided near the bottom with a cock, and pour woodvinegar over it. The iron gradually dissolves, a solution of ferrous acetate being formed, of which, after eight days, the desired quantity is drawn off.

Before adding the iron solution to the nut-gall extract, a test is made as to the quantity of vinegar required to keep the ferrous acetate in solution. For this purpose compound 1 quart of the nut-gall extract with  $\frac{1}{10}$  quart of iron solution. If a fluid, clear and dark-green in thin strata, is thereby formed, sufficient acetic acid is present. On the other hand, a black, opaque fluid indicates too little acetic acid. Now add, from a glass vessel graduated in cubic centimeters, woodvinegar—one cubic centimeter at a time—and stir after each addition. Determine how many cubic centimeters have been used for 1 quart of iron solution, and then add for every 100 quarts of nut-gall extract the corre-

sponding number of  $\frac{1}{10}$  quarts of vinegar. If, for instance, 28 cubic centimeters of vinegar have been used for 1 quart of nut-gall extract,  $28\frac{1}{10}$  quarts or 2.8 quarts of vinegar will have to be added to every 100 quarts of nut-gall extract.

This quantity of vinegar is then added to the nutgall extract, and, after dissolving the gum-arabic in it, the iron solution is poured in. In the green fluid thus formed indigo-carmine is dissolved until the ink has acquired the desired color.

Alizarin-indigo ink.—A fair alizarin ink may in a simple manner be prepared according to directions given by Prollins and Bley. Proceed as follows: Nut-galls 10, indigo 1, sulphuric acid 4, iron filings 2, chalk 2, water 80.

Boil the pulverized nut-galls with the water until the whole is reduced to 40 parts of nut-gall extract. Dissolve the indigo in the sulphuric acid (fuming sulphuric acid should be used); mix the solution with 40 parts of water, and add it to the nut-gall extract. Into this acid fluid bring the iron filings which dissolve with the evolution of gas, and the ferrous sulphate formed is at once decomposed, together with the tannin solution, ink being formed. The excess of sulphuric acid is then separated in the form of calcium sulphate (gypsum) by the chalk.

It will be observed that in this process the gypsum always shows a dark color, which is evidently caused by the gypsum carrying down a portion of the tinctorial matter. Hence it is more suitable to dissolve the iron filings in the acid indigo solution, to mix the solution formed with the chalk; then, after the gypsum is separated, to pour off the supernatant liquid, and mix it with the nut-gall decoction.

This process is quite simple, but more expensive than the ordinary method, commercial ferrous sulphate being much chcaper than that which is prepared by dissolving iron in sulphuric acid.

Alizarin ink—Indigotin 6 parts, pure water 388, sugar 20, solution of tersulphate of iron (U. S. Ph.) 62, ink body (see below) 600.

Dissolve the indigotin by one day's maceration in the water. Then add the sugar and solution of tersulphate of iron, and lastly the ink body.

In place of the ink body a solution of 60 parts of tannic acid in 540 of water may be used. The prescribed method of mixing must be scrupulously followed. The finished ink is set aside for eight days, and the clear liquid then decanted from the triffing precipitate. The ink flows bluish-green from the pen, and writing executed with it on paper soon turns black. The writing may be copied inside of the first 48 hours.

The ink body above directed to be used is prepared in the following manner :—

Macerate 200 parts of coarsely-powdered Chinese nut-galls, for twenty-four hours, in 750 parts of distilled water; strain and express. Upon the residue pour 350 parts of boiling distilled water, and express after one hour. Triturate 50 parts of white bole with the mixed strained liquids, raise once to boiling, remove the scum and filter through flannel bags. Wash the latter with water until the weight of the filtrate is 1000 parts. American alizarin ink.—Powdered nut-galls 40 parts, ferrous acetate 15, gum-arabic 10, wood-vinegar 10, indigo-carmine 5, water 100.

A number of other receipts for the preparation of alizarin inks might be given, but it is considered unnecessary, since they offer nothing new, they all containing the same raw materials, viz: a decoction of nutgalls, ferrous sulphate or another soluble iron salt, an acid and indigo solution, the only difference being in the quantities used.

Genuine alizarin ink.—Aleppo nut-galls 42, Dutch madder 3, are boiled in sufficient water to yield 120 of liquid, which is filtered and mixed with indigo-carmine 1, ferrous sulphate 5, ferrous acetate prepared with woodvinegar 2.

The addition of madder is of little importance for the durability and beauty of the ink. Besides, at the present time madder has almost entirely disappeared from commerce, the artificially-prepared alizarin being almost exclusively used for dyeing.

Hager's alizarin ink.—Bring into a very capacious porcelain dish containing 12 parts of fuming sulphuric. acid, 2 parts of indigo, in small portions; after twentyfour hours dilute the solution with 16 parts of water, and dissolve in the fluid 6 parts of iron filings free from rust.

To this fluid add the decoction of 24 parts of Chinese nut-galls, with 300 to 400 parts of water, 6 parts of gum-arabic, and 3 of sugar, and a small quantity of carbolic acid.

Since, as previously mentioned, the use of very varying quantities of tannin solution and iron salts may nevertheless yield quite good results, it is considered unnccessary to here give many similar receipts. Every intelligent manufacturer will soon find out what is wanting in the formula followed by him, and a few experiments will soon teach him the correct proportions to be used.

# Χ.

## INKS FROM EXTRACTIVE MATTER.

THAT, in directions for preparing ink, nut-galls are generally prescribed as the body which has to yield tannin is largely due to custom and to the erroneous opinion, which formerly prevailed, that the tannin contained in them differs from that occurring in other vegetable substances. It must be considered a progress that we have learned to prepare inks, in no way inferior to nut-gall ink, from a large number of vegetable substances which contain ordinary gallotannic acid or another tannin. Every manufacturer working on a large scale may procure his tannin raw material at a very cheap rate by arranging his work so as to obtain a good ink with the raw materials mentioned below.

First may be mentioned the unripe fruits of the common sloe (*Prunus spinosa*), the fruits of the common bird-cherry (*Prunus pardus*), of the elder, and in fact all fruits possessing an astringent taste or an intense coloring matter.

The barks of a majority of our forest trees also contain considerable quantities of tannin; for instance, the

bark of the oak, hemlock, elm, and willow, as well as the bark and young branches of the sumach, plum-tree, poplar, horse-chestnut, etc.

However, besides tannin, these vegetable substances also contain certain extractive matters which exert an influence upon the color of the ink, some of them yielding, with an addition of ferrous sulphate, a green ink, others a brown, and some even a purple ink. It is sought to make use of these substances in the manufacture of ink by forming from them those combinations which, in dyeing, are called "lakes."

By adding alum to a decoction of certain vegetable substances, the color of the liquid is changed, and by introducing an alkaline body, for instance, caustic potash or aqua ammonia, a combination composed of tinctorial matter and alum is separated, which is called "lake."

In the manufacture of ink it is not intended to separate the lake in the ink itself, since it being a flocculent body, it would not remain suspended in the ink, but would deposit on the bottom. It is rather sought to keep it in solution, which is effected by allowing the ink to retain a certain amount of acid.

Writing executed with such ink in a short time turns darker, the ammonia contained in the air, as well as the small quantity of lime present in the paper-substance, very likely causing the separation of the lake, and hence the writing to come out more prominently.

The quantity of alum to be used can only be learned by experience, it depending not only on the concentration of the decoction of the vegetable substances, but also on their material condition, their age, degree of ripeness, the season of the year in which they have been gathered, etc.

The correct proportion between vegetable substance and alum having been determined, as above mentioned, an ink of a green, brown, or even purple color will be obtained by the addition of ferrons sulphate. Now, indigo-carmine is also an excellent agent to correct these colors, so that with its assistance a beautiful black, blue, or permanently violet product may be obtained.

As inspissating agents, a corresponding quantity of gum-arabic or dextrin is added to the ink, and, as it is much inclined towards the formation of mould, also a small amount of carbolic acid, etc.

As previously mentioned, it is impossible to give explicit directions for all vegetable substances recommended for the manufacture of ink, and only a few of them will here be mentioned, in order to give the manufacturer an idea of the course to pursue.

Sambucin ink.—The berries of the elder (Sambucus ebulus) contain a considerable quantity of a reddish-blue tinctorial matter, and yield a very good ink. The writing executed with this ink is at first violet, but soon turns black. The ink is prepared according to the following formula: Elderberries 100, ferrous snlphate 5, alum 2, vinegar 5.

Bruise the ripe berries, express the juice, and mix it with the vinegar; then add to the red fluid the alum and ferrous sulphate previously dissolved in hot water.

Sloe ink.—Sloes 200, ferrous sulphate 10, alum 4, vinegar 50, water 125.

Boil the bruised unripe sloes with the water, add to the strained decoction the vinegar, and finally the solu-

### THE MANUFACTURE OF INK.

tions of the ferrous sulphate and alum. The addition of a small quantity of carbolic acid protects this and similar inks from becoming mouldy.

Chestnut ink.—The prickly shells enclosing the fruits of the horse-chestnut (Æsculus hypocastanum) yield, when boiled, a very useful extract for the preparation of ink. Use: Green shells 200, ferrous sulphate 2, alum 1, water 1000.

Boil the shells with the water, for a few hours, strain the decoction and mix it with the ferrous sulphate and alum solution. Very cheap and good inks may, in the same manner, be prepared from the bark of the young branches of the horse-chestnut.

Catechu ink.—Catechu 10, ferrous sulphate 10, gumarabic 2, water 100.

Dissolve the catechu in boiling water, allow the solution to clarify by standing, and then mix it with the ferrous sulphate. By means of catechu an excellent ink may in a short time be prepared, which is still further improved by the addition of a few per cent. of strong vinegar.

Juglandin ink.—The green pulp which surrounds the fruits of the walnut tree (Juglans regia) contains an extractive matter which rapidly turns brown in the air, and imparts an intense color to the skin. This extractive matter yields a very durable and beautiful black ink, according to the following formula: Green walnut shells 100, ferrous sulphate 4, alum 1, water 400.

# XI.

## LOGWOOD INKS.

Logwood or Campeachy wood (*Hæmatoxylon campechianum*) contains a tinctorial matter which is soluble in water, and shows a very characteristic behavior towards certain reagents. The aqueous decoction of the wood, as well as the extract prepared at the ordinary temperature, has a red color, which, however, rapidly turns blue by the addition of alkalies (potash lye). Pure hæmatoxylin—the coloring matter of logwood—forms colorless or pale yellow crystals, but is converted into rcd hæmatin by the wood being exposed for sometime to the air,

With ammonia, hæmatin forms a combination of a violet color; when compounded with solution of alum or of lead acetate (sugar of lead), and then mixed with ammonia, it yields blue or violet precipitates (lakes).

Of the greatest importance for our purposes is the behavior of a decoction of logwood or a solution of the extract towards chromates, it yielding, when brought in contact with neutral chromates, a very dark-colored fluid, which may be used as ink or for dyeing.

On account of this property, logwood, as well as logwood extract, is much used in the manufacture of ink. The inks prepared with their assistance are distinguished by a beautiful color, considerable durability, and cheap cost of production.

English logwood ink.—Nut-galls 100, logwood 120, ferrous sulphate 35, gum-arabic 100, vinegar 400, water 500.

### THE MANUFACTURE OF INK.

This ink may directly be prepared by bringing the ingredients into a barrel, and stirring at least once a day. In the course of about ten to fifteen days the ink has acquired a sufficiently black color to be filled in bottles. When the liquid has been drawn off, add to the residue, which consists of remains of nut-galls and logwood, ferrous sulphate 15, gum-arabic 30, vinegar 100, water 150. The fluid thus obtained is quite a good ink. With one-half of the quantities just mentioned, the residue of the materials yields, even for the third time, ink, which, as regards color, is, however, inferior to the first two products.

For the preparation of this ink it is also recommended to suspend the materials in a linen bag, in the barrel, the ink thus obtained being free from solid bodies pieces of wood or of nut-galls.

The chief disadvantage of this very convenient method of preparing ink is that the product readily moulds, whereby its tinctorial power is injured. To overcome this disadvantage it suffices to substitute for the ordinary vinegar, wood-vinegar, which, as previously stated, contains enough carbolic acid to prevent the formation of mould. If wood-vinegar cannot be had, add a small quantity of carbolic acid to the ink.

If it is desired to produce this ink within a few hours, it is only necessary to assist the solution of the ingredients by boiling. In this case the nut-galls should be reduced to a coarse powder, and the logwood to raspings or very fine shavings.

French logwood ink.—Nut-galls 55, logwood 30, ferrous sulphate 30, cupric sulphate (blue vitriol) 8, alum 2, gum-arabic 20, water 1500.

Pour the water over the pulverized nut-galls and the logwood reduced to fine shavings, and heat to boiling. Continue boiling until the fluid is reduced to one-half the quantity, then strain the boiling fluid, and dissolve in the clear liquid the finely-powdered ferrous sulphate. cupric sulphate, alum, and gum-arabic. The fluid can at once be used as ink, but it is best to let it stand for a few days, and then decant it from any sediment which may have formed. The latter is returned to the boiler containing the exhausted nut-galls and logwood shavings. and the following ingredients are added: Ferrous sulphate 10, cupric sulphate 2, gum-arabic 8, water 500. Boil the whole for two hours, and filter the resulting fluid while boiling hot. The ink thus obtained, though inferior to the first product, is superior to many nutgall inks. Like all other logwood inks, it has the advantage of containing no free acids, and, hence, of leaving the steel-pens entirely unchanged.

A steel-pen used for writing with this ink until the point became so dull that it was impossible to make a fine stroke with it, was, after removing the adhering crust by soaking in water, perfectly smooth and bright, which would certainly not have been the case if the ink had been acid and attacked the steel.

Germania ink.—Nut-galls 100, logwood extract 15, ferrous sulphate 30, alum 2, vinegar 5, carbolic acid 1, water 1200.

This ink is prepared as follows: Pour 1000 parts of water over the pulverized nut-galls in a vat which, immediately above the bottom, is provided with a cock. (Cover the vat and let it stand quietly for 14 days.

At the same time dissolve in another vessel the log-

wood extract in 100 parts of water, and the ferrous sulphate and alum in the remaining 100 parts.

When the liquid has been drawn off from the nutgalls (considerable mould is generally formed upon the mass in the barrel), add to it the carbolic acid and vinegar, and finally stir in the solutions of the ferrous sulphate and alum. The product thus obtained is of an intense color, and is distinguished by great fluidity, in consequence of which it penetrates deeply into the paper and is difficult to efface by chemical agents, making it especially suitable for the execution of important documents.

Logwood ink containing gallic acid.—Although, as seen from the description of its fabrication, Germania ink contains partially gallic acid, the process may be so conducted as to combine all the advantages of a good alizarin ink with those of a logwood ink. Such ink is prepared according to the following formula :—

Nut-galls 100, ferrous sulphate 30, vinegar 800, earbolic acid 1.

Pour sufficient water over the nut-galls to thoroughly moisten them and let them stand for three weeks, during which time an abundance of mould is formed and all the gallotannic acid is converted into gallic acid. Then add the vinegar, and, after thoroughly stirring the mass, strain off the fluid.

Upon the residue of the nut-galls pour water to displace the vinegar, and let the fluid run off until 800 parts are obtained. In a portion of this fluid dissolve by boiling 20 parts of logwood extract and 1 of alum, and add the hot solution to the first fluid. Finally add the carbolic acid to the finished ink.

As will be seen from the above description, a gallic acid ink is at first obtained, which, if used by itself, yields greenish writing, becoming black after exposure to the air. However, by the addition of the solution of logwood extract, an ink is obtained which immediately yields writing of an agreeable blue-black color, which in a short time changes to a beautiful, lustrous, intense black.

Besides small cost of production, all the logwood inks above mentioned have the advantage of penetrating deeply into the paper, which is a guarantee for the stability of the writing executed with them.

Chrome logwood inks.—All the inks previously deseribed consist, without exception, of very finelydivided precipitates, suspended, as in the ordinary nut-gall inks, in a clear liquid, or of fluids in which these precipitates are kept in solution by an acid acctic or sulphuric acid; but none of these inks actually consists of a black fluid which, by standing quietly, would not deposit a precipitate.

There is, however, a fluid which is nothing but a black liquid mass, containing no solid body in suspension, nor being kept in solution by acids. The chemist Runge, who discovered this fluid, found that the neutral chromates possess the property of forming with a decoction of logwood—or, what is virtually the same, with a solution of logwood extract in water—a liquid of an intense black color. As the most suitable salt for the purpose, he recommended chromate of potassium. This salt being sold at a high price, though its manufacture requires no special skill, directions for preparing it are here given :—

#### THE MANUFACTURE OF INK.

Preparation of chromate of potassium.—Dissolve 1 part of commercial bichromate of potassium in 10 parts of water, heat the solution to boiling, and add pulverized potash until the effervescence caused by the escape of carbonic acid ceases. A slight excess of potash is not injurious. The fluid gradually changes its originally yellowish-red color to yellow. The solution is then reduced to one-half the quantity by evaporating, and finally stirred until cold. In cooling, small yellow crystals of chromate of potassium are formed, which, after decanting the fluid from them, are dried between blotting-paper. The fluid decanted off may be used instead of water for dissolving fresh quantities of bichromate of potassium.

The chemical process which takes place on bringing a solution of the tinctorial matter of logwood in contact with chromate of potassium is not yet thoroughly understood, some chemists holding the opinion that a combination consisting of chromic oxide and the tinctorial matter is formed. Although several combinations, consisting of metallic oxides and organic dye-stuffs, are known, it would seem that the above-stated view is not correct. An exceedingly small quantity of chromate of potassium suffices to change a considerable quantity of logwood decoction into ink; but the proportion of chromium to the hæmatin dissolved in the fluid is so exceedingly small that the formation of a chemical combination is not probable, though not impossible.

It has been found that the quantity of chromate of potassium required for the conversion of a certain amount of logwood decoction into ink varies very

much, this surprising phenomenon being very likely due to the varying quantities of tinctorial matter in the different varieties of logwood. Furthermore, it has been found that it makes considerable difference whether too little or too much chromate of potassium is used. In the first case, the ink does not acquire the desired sad color; while in the latter, though of a beautiful black color, it is liable to turn brown.

From what has been said, it will be seen that definite proportions regarding the quantities of chromate of potassium and logwood decoction cannot be given, although, by working according to the process given below, a constantly uniform and excellent ink may be prepared.

Two fluids are prepared, namely : No. 1, from 40 lbs. of logwood and 120 quarts of water; and No. 2, from 2 lbs. of chromate of potassium and 10 quarts of water.

The logwood, converted into fine shavings, is boiled with the water until about <sup>1</sup> is evaporated, so that the residue amounts to about 100 quarts. The decoction, which has a beautiful red color, is strained through a cloth and collected in a vat.

Now add to this fluid  $\frac{1}{10}$  quart of the chromate of potassium solution, stir thoroughly, and bring a sample into a test-tube. If the fluid still transmits light, or writing executed with it shows a violet or even a reddish color, more chromate of potassium has to be added until the color of the fluid has become pure black and writing executed with it at once appears blue-black.

As a guide for future operations, the samples of writing are preserved, noting at the same time the proportions between chromate of potassium and logwood decoction. After lying for some time, a comparison of the different writings will indicate the proper proportions.

Chrome ink with logwood extract.—The most convenient and simple method is to prepare the chrome ink with logwood extract, as follows : Logwood extract 2 lbs., chromate of potassium  $2\frac{1}{2}$  drachms, water 50 quarts.

Dissolve the chromate of potassium in the water, and suspend the comminuted logwood extract tied in a linen cloth in the fluid. The extract immediately dissolves, a deep black ink being formed.

Chrome inks prepared with decoction of logwood or logwood extract are distinguished by many valuable properties: they are very cheap, of a beautiful black color and durable.

Violet logwood ink.-Logwood 100, alum 5, gumarabic 10, water 500.

Boil the logwood with the water, dissolve the gum in the hot fluid, and finally add the alum, previously dissolved in hot water. If ink of a more purple shade is desired, decrease the quantity of alum  $\frac{3}{5}$  or  $\frac{1}{2}$ , and if the ink is to show a blue-black color with only a violet tinge, carefully add a small quantity of chromate of potassium solution.

Thinly-fluid logwood ink.—Solution of logwood extract 110 lbs., dextrin 20, water 135 quarts, alum 18 lbs, sulphuric acid 1.5, chromate of potassium 0.75.

The sulphuric acid is mixed with the fluid before adding the alum and chromate of potassium.

Ordinary logwood ink.—Logwood extract  $35\frac{1}{2}$  ozs., dextrin 1 oz., alum 21 ozs., water 80 quarts.

The alum is added after the solution of all the other ingredients.

Good logwood ink.—Dissolve logwood extract 60 parts in water 500 parts. Add to the solution crystallized carbonate of soda 16 parts, and glycerin (of specific gravity 1.25) 60 parts, and finally potassium chromate 2 parts, and gum-arabic 16 parts, reduced to a powder and dissolved in water. This ink does not attack pens, does not become mouldy, and is very black.

Violet logwood ink.—Solution of logwood extract 300 quarts, alum 24 lbs., dextrin 30 lbs.

Dissolve the alum with the assistance of heat in a portion of the extract solution, and, after adding this solution to the rest, suspend in the fluid about 4 ozs. of finely-pulverized acetate of copper tied in a small linen bag.

Red logwood ink.—Solution of logwood extract 500 quarts, dextrin 50 lbs., alum 25 lbs., acetate of copper 7 ozs.

To this fluid add, in small portions of about 5 drachms each, sulphuric acid until the ink shows the desired red color. Stir thoroughly after each addition of acid. This ink attacks steel-pens, but not overly much, if the pen, after being once used, is allowed to dry without wiping.

# XII.

#### COPYING INKS.

THE quality required of a copying ink is that it shall remain moist for sometime, and afford one or more copies of the written matter by applying dry or dampened paper to its surface, and subjecting it to more or less pressure. This property is imparted to the ink by the addition of so-called hygroscopic substances, which possess the property of constantly absorbing moisture from the air.

As hygroscopic substances, sugar, dextrin, grapesugar (glucose), or small quantities of crystallized calcium chloride, which forms a very deliquescent salt, are used. An excess of hygroscopic substance would, however, be injurious, since the original writing would remain too damp, and blot even after lying for sometime.

By sufficiently inspissating any one of the inks described in the preceding sections, and adding a corresponding quantity of hygroscopic substances, it can be changed into a copying ink.

Inks which, like the ordinary nut-gall inks, consist of a dark precipitate suspended in a liquid, are less suitable for copying inks than those in which the tinctorial matter is dissolved, as is the case with alizarin and logwood inks.

Ordinary gallic acid copying ink.—Nut-galls 120, ferrous sulphate 30, gum-arabic 20, glucose 10, water 1000.

In this ink the glucose is the ingredient which absorbs

the water. But since glucose solutions are readily decomposed, and the ink in consequence would soon spoil, decomposition is prevented by the addition of a small quantity of carbolic acid. If in copying this ink should prove too sticky, it may be mixed with a suitable quantity of another ink, which contains neither gum-arabic nor glucose.

Double gallic acid copying ink.—Nut-galls 70, ferrous sulphate 70, logwood 160, gum-arabic 50, glucose 20, water 600, vinegar 100.

Instead of logwood, 16 to 18 parts of logwood extract may be used. Even a larger quantity of the extract is not injurious, it being very hygroscopic, and thus contributes to the writing remaining moist.

Logwood copying ink.—Logwood extract 100, ferrous sulphate 2, cupric sulphate (blue vitriol) 1, alum 12, glucose 8, chromate of potassium 1, indigo-carmine 19, water 500.

Dissolve the logwood extract, glucose, and indigo-carmine in 400 parts of water, and the salts in the remaining 100 parts; finally mix the two fluids by thorough stirring.

*Glycerin copying ink.*—Logwood extract 100, ferrous sulphate 4, chromate of potassium 1, indigo-carmine 8, glycerin 10, water 500.

This excellent ink is prepared by dissolving the logwood extract, ferrous sulphate, and chromate of potassium in water, and adding to the solution the glycerin and indigo-carmine. This ink being quite thinly-fluid, very fine writing can be executed with it, since it penetrates deeply into the paper and remains moist for sometime. Many copies of the writing can be made. Boettger's copying ink.—Logwood extract 64, soda 16, chromate of potassium 24, glycerin 64, gum-arabic 16, water 270.

Dissolve the logwood extract together with the soda in water, add the glycerin and gum-arabic, and finally, with constant stirring, the chromate of potassium, previously dissolved in a small quantity of hot water.

By simply pressing with the hand, three copies can be taken from the original writing when just finished, and two more with the assistance of a copying press.

Logwood copying ink.—Logwood extract  $2\frac{1}{4}$  ozs., vinegar 2 lbs., water 2 lbs., ferrous sulphate  $1\frac{1}{4}$  ozs., alum 11 drachms, gum-arabic 1 oz., sugar 2 ozs., glycerin 1 to 3 drachms.

Birmingham copying ink.—Solution of logwood extract 650 lbs., dextrin 30, alum 33, verdigris 0.25, oxalic acid 2, glycerin 7 to 21.

Allfield's copying ink.—(For copying without the use of a press.) Evaporate 10 volumes of ordinary ink to 6 volumes, and add 4 volumes of glycerin. The writing executed with this ink can be copied by simply laying the copying paper upon it, but it readily blots.

Violet-blue copying ink.—Extract of logwood 60 parts, oxalate of ammonium 50, sulphate of aluminium 10, sugar 10, oxalic acid 3, bichromate of potassium 6, salicylic acid 1, pure water as much as required.

Reduce the first five ingredients to a coarse powder, and heat the mixture with 800 parts of water to boiling. Then add a solution of the bichromate of potassium in 150 parts of hot water, next add the salicylic acid and set the whole aside for fourteen days. Pour off the clear liquid and fill it in bottles.

This ink is violet-blue in thin layers, flows dark-blue from the pen, and yields bluish-black copies.

Knaffl's copying ink.—This ink is of special value to architects and engineers, since, without moistening the original drawing or the copying paper, it yields copies of such sharpness that the finest lincs of the original are reproduced. To be sure, the ink is rather expensive, but that is of but little importance, since from drawings, building plans, etc., executed with it, two or three copies can be readily produced. The ink is prepared according to the following formula :—

Solution of pyrogallic acid 240, cupric sulphate (green vitriol) 4, ferric chloride 10, acetate of uranium 2.

As will be seen, the materials used in the preparation of this copying ink differ very much from those usually employed. The pyrogallic acid may be prepared according to the methods given on p. 31, but as it is much used in photography it can at present be bought at a comparatively low price.

The acetate of uranium is somewhat more expensive, but since it is used in porcelain painting its price has been somewhat reduced.

Ferric chloride may readily be made by preparing a saturated solution of iron in 10 parts of hydrochloric acid, mixing it with 1 part of strong nitric acid and evaporating it in a porcelain dish until crystals commence to separate. The dark-brown solution of ferric chloride is then kept in well-closed glass bottles.

If a copy is to be made of a drawing, plan, etc., executed with this ink, place a sheet of thick, very smooth

#### THE MANUFACTURE OF INK.

paper (bristol board is very suitable for the purpose) upon the original, cover it with a smooth board and uniformly load the latter with books, without, however, using specially strong pressure. In the course of three to five days the drawing will be reproduced in its original sharpness. A second and even a third copy may in the same manner be made.

Red copying ink.—Extract of logwood 100 parts, oxalate of ammonium 30, sulphate of aluminium 30, oxalic acid 8, bichromate of potassium 5, salicylic acid 1, pure water 950.

Reduce the first four ingredients to a coarse powder and heat the mixture with 800 parts of the water to boiling in a copper vessel. Then add a solution of the bichromate of potassium in the remaining 150 parts of water, heated almost to boiling, next add the salicylic acid, and set the whole aside for 14 days. Pour off the clear liquid and fill it in bottles.

In thin layers this ink has a fine red tint and writes with a violet-red color, which copies dark violet and also assumes the last-mentioned shade when drying. It is one of the best copying inks in existence. Writing done with it can be copied many weeks afterwards.

Inks which yield copies without a press.—I. Black.— Nigrosine 20 ozs., glucose 3 ozs., hot water  $3\frac{1}{2}$  pints, glycerin  $2\frac{1}{2}$  ozs.

To the solution of the nigrosine in the hot water add the other ingredients and strain through a piece of silk. If too thick when cold, dilute to the proper consistency with water.

II. *Blue.*—Cotton blue (anilinc) CB 12 ozs., glucose 2 ozs., glycerin  $\frac{1}{2}$  oz., hot water 2 quarts.

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Proceed as directed for black ink (above). In preparing these inks it is absolutely necessary that the water should be kept hot while dissolving the tinctorial matter. Solution is best effected by trituration, which should be continued until all the dye has been taken up by the water. The straining must be performed hot, otherwise the filtering-cloth quickly becomes clogged.

Copying water.—Dissolve 1 part of chromate of potassium in 1000 parts of water.

With the use of this composition excellent copies may be obtained, even from writings several years old, which are entirely indifferent to ordinary water.

# XIII.

## THE HEKTOGRAPH AND HEKTOGRAPH INKS.

I. The hektograph.—The hektograph or copying pad is very useful in copying writings or drawings when only a limited number of copies is required. A practical hektograph may be prepared according to the following directions :—

Soak a good quality of glue—so-called gilder's glue for 24 hours in sufficient cold water to cover it. Then take the swelled glue from the water and melt it in an enamelled pot over a moderate fire. When the glue is perfectly liquid add the required quantity of glycerin (see directions for hektograph masses later on), and intimately mix both by continued stirring.

The vessel containing the mixture should for sometime be kept hot, so that the mass remains thinly-fluid.

The purpose of this is to allow the air-bubbles formed by stirring to rise to the surface. If any scum is formed on the surface remove it carefully with a shallow spoon. The composition is then ready to be poured into the vessel intended for its reception, which may be made especially for the purpose or a shallow baking pan of tin may be used. When the pan is filled with the composition place it in a level position in a cool place free from dust, and allow it to remain at least for several hours.

To prepare the pad for use, pass a wet sponge lightly over the face of the composition, and allow it to become nearly dry before taking the first copy. If this precaution is neglected, the face of the pad will be ruined by the first transfer.

The writing or drawing to be copied must be made with hektograph ink (see below), using a new steel-pen. After the writing becomes dry it is placed face down on the pad, and rubbed gently on the back to insure the perfect contact of every part. After remaining on the pad for about a minute, remove the original and proceed to take the copies by placing the paper on the pad, and removing it therefrom, always beginning at the corner.

After taking the desired number of copies, or when the impression is exhausted, the pad is washed lightly with a sponge wet with cold water. The pad is then allowed to dry before being again used.

The correct constitution of the hektograph mass can only be determined by copying experiments. If the mass has been too much evaporated, and is consequently not sufficiently elastic and sticky, the hektograph will

### THE HEKTOGRAPH AND HEKTOGRAPH INKS. 99

yield but a small number of copies. This defect may be remedied by stirring hot water into the mass. If, on the other hand, the mass has not been sufficiently evaporated, and it is very elastic, and so sticky that the paper can only be withdrawn from it with difficulty, the hektograph yields blotted and indistinct copies. To remedy this defect, withdraw water from the mass by evaporating it.

According to some directions, white pulverulent substances are mixed with the actual hektograph mass, consisting of glue and glycerin. The object of such additions, whose behavior is entirely indifferent, is simply to color the mass white, so that the writing upon it may be more plainly seen, and to increase the volume of the mass. These substances may, of course, be omitted.

Directions for the preparation of hektograph masses. Ordinary hektograph mass.—I. Gilder's glue 100, glycerin of 28° Bé. 500.

The glue is allowed to swell in water, as described above, then melted, mixed with the glycerin, and evaporated to the required consistency.

II. Gilder's glue 100, glycerin of 28° Bé. 400, water 200.

Chromograph masses.—The writing transferred to the hektograph can be more readily removed by washing, when indifferent bodies in a finely-divided state arc mixed with the above-mentioned substances, freshlyprecipitated barium sulphate being especially suitable for that purpose. It is prepared by dissolving barium chloride in water, and adding to the solution sulphuric acid, as long as a precipitate is formed. The fluid is then decanted from the precipitate, the latter stirred up with water, and allowed to settle, when the water is poured off, and the same operation several times repeated. The white mass remaining in the vessel is used in a moist state.

I. Gelatine 100 parts, dextrin 100 parts, glycerin 1000 parts, barium sulphate as much as required.

The heated mass is stirred until all the glue and dextrin are dissolved. It is then allowed to cool somewhat, and poured into tin pans. If not a sufficient number of copies are obtained, or the mass is cleansed with difficulty by washing, add more glycerin.

II. Good ordinary glue 100 parts, glycerin 50, barium sulphate 25, water 375.

III. (Recommended by the French Ministry of Public Works.) Glue 100 parts, glycerin 500, finelypowdered barium sulphate or elutriated kaolin 25, water 375.

For ink a concentrated solution of aniline violet (violet de Paris) is recommended.

Hektograph sheets.—Soak 4 parts of best white glue in a mixture of 5 parts of water and 3 parts of solution of ammonia, until the glue is soft. Warm the mixture until the glue is dissolved, and add 3 parts of granulated sugar, and 8 parts of glycerin, stirring well, and letting come to the boiling point. While hot paint it upon white blotting-paper with a broad copying brush, until the paper is thoroughly soaked, and a thin coating remains on the surface. Allow it to dry for two or three days, and it is then ready for use. An aniline ink should be used for writing, and before transferring to the blotting-paper, wet the latter with a damp sponge,

## THE HEKTOGRAPH AND HEKTOGRAPH INKS. 101

and allow it to stand one or two minutes. Then proceed to make copies in the ordinary way. If the sheets are laid aside for two days, the old writing sinks in and does not require to be washed off.

II. Hektograph inks.—For the preparation of these inks a powerful and intense tinctorial matter and a sufficient quantity of glycerin are required. Among the known dye-stuffs, the aniline colors possess the greatest tinctorial power, and they are, therefore, exclusively used for the purpose. Many of the hektograph . inks brought into commerce are quite thickly-fluid, which makes writing with them disagreeable work. This is due to the fact that the majority of aniline colors are soluble with sufficient ease only in alcohol, and in order to obtain intense solutions very strong alcohol is used. Now, during writing a considerable portion of the alcohol evaporates from the pen, in consequence of which the ink becomes thick.

However, at present, several aniline colors soluble in water are known, especially the blue and red varieties, which are of importance for the preparation of ink, possessing this property. Writing with such ink has no disagreeable features, and it is, therefore, recommended to use only aniline colors soluble in water in the preparation of hektograph inks.

However, by skillful manipulation, aniline colors not soluble in water may be incorporated with the ink by the use of a very small quantity of alcohol, such ink not drying so rapidly in writing.

Bring the weighed-off quantity of aniline into a porcelain mortar, pour over it the required quantity of glycerin, place the mortar upon a stove heated to from 104° to 122° F., and triturate the glycerin with the aniline. The aniline colors are soluble in glycerin, and much more readily so when the latter is heated. If the mass is too viscous to be stirred with ease, add water so that a fluid of the consistency of syrup is formed. Trituration is then continued until a solid body is no longer felt with the pestle. The tinctorial matter is then kept in solution by carefully diluting with 50 per cent. alcohol. By this process very useful hektograph inks can, for instance, be prepared from methyl violet, which is insoluble in water.

Blue hektograph ink.—Heat in a suitable vessel, with constant stirring, 10 parts, by weight, of aniline blue soluble in water, 10 of glycerin, and 50 to 100 of water. Solution takes place immediately, and, according to the quantity of water used, an ink is obtained which permits the taking of a smaller or larger number of copies. On account of its fluidity, the finest pen-drawings may be executed with this ink, and copies of them taken by means of the hektograph.

Methyl violet ink.—I. Mcthyl violet 10 parts by weight, dilute acetic acid 5, alcohol (90 per cent.) 10, water 10, glycerin 5.

II. Methyl violet 10 parts by weight, alcohol 10, gum-arabic 10, water 70.

Heat the ingredients in a glass flask to from  $122^{\circ}$  to  $140^{\circ}$  F. for 2 hours, and then filter the solution through flannel.

Red hektograph ink.—I. Diamond fuchsine 10 parts by weight, alcohol 10, acetic acid 2.5, gum-arabic 10, water 70.

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II. Diamond fuchsine 10 parts by weight, alcohol 10, glycerin 10, water 50.

Proceed for both inks as directed for methyl-violet ink II. The second formula yields a beautiful copying ink.

Violet hektograph ink.—By mixing a blue and a red hektograph ink, violet in all desired shades may be obtained. The ink prepared from aniline blue, soluble in water, and the red ink II. (above) are especially suitable for the purpose.

Green hektograph ink.—Aniline blue, soluble in water, 10 parts by weight, picric acid 10, alcohol (90 per cent.) 30, glycerin 10, water 30.

By decreasing or increasing the quantity of pieric acid, various shades of yellow are obtained.

Black hektograph ink.—Aniline black or nigrosine is insoluble in water, and hence black hektograph ink is prepared by triturating very dark methyl violet with nigrosine, and treating the mixture with alcohol and glycerin.

Methyl violet 10 parts by weight, nigrosine 20, alcohol 60, glycerin 30, gum-arabic 5.

This ink is very thickly-fluid, the nigrosine not being dissolved in it, but simply divided. As previously mentioned, the best hektograph inks are those which represent actual solutions, and, amongst them, especially the preparations from aniline colors soluble in water. Later on, when discussing the aniline inks, this important subject will be referred to.

# XIV.

### SAFETY INKS.

FOR many years chemists have endeavored to invent an absolutely inextinguishable ink, which can only be destroyed together with the paper, parchment, etc., upon which it is deposited. The value of such an ink for important documents, etc., will be readily understood.

However, a formula for preparing an ink which would completely resist all chemical influences cannot be given, for a skillful chemist, willing to spend the necessary time and patience, can, without leaving any traces, efface any writing executed with ink.

To be sure, there is a substance which resists all chemical agents, and is not dissolved by any known solvent. This substance is finely-divided carbon, which occurs in commerce under the name of lamp-black. However. an ink prepared with it does not deeply penetrate into the paper. The fibre of the paper does not absorb the dark fluid, the particles of carbon simply depositing themselves mechanically upon the surface so that they can be almost completely removed by careful washing with water. Printing ink alone forms an exception. It is prepared by intimately triturating finely-divided carbon with varnish. By reason of this content of varnish the printing ink penetrates so deeply into the paper that, especially if the latter is porous, the characters printed upon it cannot be entirely effaced with any known solvent. However, printing ink is unfortunately of such

a consistency that it cannot be used for writing, it being too thickly-fluid to flow with sufficient ease from the pen.

Among the black pigments prepared with the assistance of carbon, genuine Chinese or India ink contains the carbon in the finest possible state of division. But, as shown by direct experiments, writing executed, even years ago, with Chinese ink, can be removed by carefully soaking the paper in water, and washing with a soft sponge.

The durability of writing depends less on the resistance offered by the ink to chemical agents than on the deep penetration of the ink into the paper. Hence, writing executed with thinly-fluid inks upon soft porous paper will be more resistant than that with inks containing solid bodies.

Ordinary alizarin inks containing quite a large quantity of indigo-carmine are difficult to remove, especially if the paper is porous, so that the writing soaks through. Of extraordinary resistance are inks which chiefly consist of certain dark-colored, vegetable, extractive substances rich in humin bodies.

By writing, for instance, with a solution of glucose mixed with about 1 per cent. of caustic potash or soda, pale-brown writing ink is at first obtained, which, however, constantly becomes darker and energetically resists the action of acids and alkalies, and even that of chlorine. This is due to the fact that all these bodies only effect a further decomposition of the humin substances, bodies richer in carbon, and hence of a darker color, being thereby constantly formed.

There are many compositions recommended as safety

inks, some of them actually affording considerable security, though none of them can resist the manipulations of a skilled chemist.

Document safety ink.—Shellac 15, borax 8, gum-arabic 8, lamp-black 10, water 130.

This ink is prepared by adding the water to the shellac and borax, both finely pulverized, and boiling with constant stirring, until all the shellac is dissolved. The solution is filtered through blotting-paper. In the meanwhile the gum-arabic is converted into a fine powder, and intimately mixed with the lamp-black in a mortar. The mixture is then brought into the pot used for boiling the shellac, borax and water, and after pouring some of the filtered fluid over it, heated to boiling. When all the gum-arabic is dissolved, gradually add, with constant stirring, the rest of the fluid, and set the whole aside for a few days to allow the coarser particles of the lamp-black to settle. The finished ink is carefully decanted or siphoned off from the sediment.

The constituents of the shellac suffer by the action of the boric acid—contained in the borax—a far-reaching change, in consequence of which combinations of a deep brown color are formed from the resin, which offer such resistance to chemicals that the complete destruction of the writing executed with the ink cannot be effected without so strongly attacking the paper as to make detection easy.

A very resistant writing fluid is also obtained by simply boiling shellac with water, the lamp-black being only added to impart a darker color to the ink. As a substitute for the lamp-black, the decoction of shellac and borax may, after filtering, be mixed with a corresponding quantity of indigo-carmine, or of a very concentrated logwood chrome ink.

Read's safety ink.—The actually effective constituent of this ink is the so-called soluble Berlin or Prussian blue. The ink is prepared by dissolving ordinary Berlin blue in oxalic acid. The best dark-blue quality of Berlin blue should be used, the cheaper varieties being frequently adulterated with foreign substances—for instance, with chalk.

For the ready solution of Berlin blue in oxalic acid, it must first be converted into *prepared* Berlin blue, which is effected by bringing it into a capacious porcelain dish and pouring over it an equal quantity of sulphuric acid and allowing the whole to stand for 8 days. The sulphuric acid is then poured off, and after bringing the contents of the dish into a larger vessel and pouring water over them, the whole is thoroughly stirred and then allowed to settle. This operation of washing is repeated until the water poured off shows not the slightest acid taste. The solution of oxalic acid is poured upon the moist prepared Berlin blue, the proportions generally used being 5 parts of Berlin blue and 1 part of oxalic acid dissolved in 5 parts of water.

The resulting clear fluid is poured off from the portion remaining undissolved and mixed with an equal quantity of good logwood chrome ink.

If the writing executed with this ink is allowed to dry slowly, it penetrates very deeply into the paper, and the more deeply it penetrates, the more difficult it is to remove.

Resin safety ink.—Common rosin 10, crystallized soda 10, lamp-black 2, gum-arabic 4, water 100. This very cheap and at the same time good safety ink is prepared by boiling the rosin with the soda and water until a clear solution is formed, which may be accelerated by using, instead of 10 parts of soda, a mixture of 7 parts soda and 3 of caustic lye. The gumarabic is triturated with the lamp-black, the mixture diluted with water and added to the rosin solution.

Water-glass ink.—According to the formula of its inventor, M. Baudrimont, this excellent safety ink is prepared as follows:—

Potash water-glass 20, lamp-black 2.

In commerce potash water-glass occurs in the form of a thick viscous fluid, which has to be protected from the access of air, it otherwise being in a short time converted into a solid glass-like mass. Triturate the lamp-black with a small quantity of the water-glass until a uniform paste is formed, and mix this paste with the remaining water-glass. The black fluid thus obtained is immediately brought into small bottles and the latter hermetically closed.

In writing, the silicic acid contained in the water-glass separates from the ink, which penetrates deeply into the paper, and at the same time envelops the particles of carbon of the lamp-black, thus producing writing which resists all attacks.

Since, however, the potassium separated by the oxygen of the air might, in the course of time, injure the paper, it is recommended to remove it from writing intended to be preserved for a long time. This is effected by, for a few hours, placing the paper upon which the writing has been executed in water slightly acidulated with vinegar and then washing with pure water until every trace of acid is removed.

Carbon safety ink.—The ink known under this name is actually nothing but a sort of pigment held in solution. It is prepared by triturating lamp-black 10 parts by weight, gum-arabic 10, and oxálic acid 5, with water 200. Use but little water at first, adding the rest when the thick mass has become quite uniform.

Writing executed with this and similar inks has the defect of penetrating but slightly into the paper. By reason of their content of carbon they absolutely resist the action of the most powerful chemicals, but, as proved by special experiments, they can, without leaving scarcely any traces, be removed from the paper by careful treatment with water.

Vanadium ink.—This ink, invented by the celebrated chemist Berzelius, is prepared by adding to a filtered decoction of nut-galls ammonium vanadate, which is rather expensive and but seldom occurs in commerce. However, the question of expense is nothing in comparison to the action of this salt, which is still more energetic than that of chromate of potassium upon logwood decoction, a few drops of ammonium vanadate solution sufficing for the conversion of a considerable quantity of nut-gall decoction into a deep-black ink, which is distinguished by excellent fluidity.

Vanadium ink cannot be destroyed by any known agents, the writing always remaining plainly legible; and, hence, it would decidedly be the best safety ink if the ammonium vanadate required for its preparation could be more readily obtained in commerce.

## XV.

## INK EXTRACTS AND INK POWDERS.

It has been repeatedly tried to bring into commerce preparations which contain the ink in a compact form and permit the direct production of a good ink by simply mixing with water. Although some of these preparations yield good results and their form is extremely handy for carrying ink along on a journey, especially on routes where accommodations have to be mainly provided by the traveller himself, the demand for them is rather limited.

Ink extracts.—Ink extracts may be readily prepared by evaporating ink to a certain degree and filling the concentrated solution in bottles. The mode of operation varies, however, according to whether extracts of inks containing gallotannic or gallic acid are to be prepared, or of alizarin and logwood chrome ink.

In the first case, it is best to evaporate in a shallow pan, without heating to boiling, the nut-gall decoction by itself until only about one-quarter of the original fluid remains, and to dissolve in this fluid the other constituents, ferrous sulphate, gum-arabic, etc. To prepare ink from this thickly-fluid extract, it is only necessary to mix it with five to eight times the quantity of water.

For making alizarin ink extract, prepare an alizarin ink according to one of the directions previously given, and carefully evaporate it in a large shallow porcelain dish. Neither iron nor copper vessels should be used for this purpose, as they are strongly attacked by the free acetic acid present.

If it is observed that in consequence of the evaporation of too much acetic acid the fluid would no longer form a clear solution, add a small quantity of strong acetic acid. By evaporating at a low heat and adding a small quantity of acetic acid, alizarin ink may be highly concentrated, so that a small quantity of extract will yield a considerable quantity of ink by the addition of water.

Logwood chrome ink and chestnut ink may be evaporated to a very thickly-fluid extract without in the least injuring the quality of the ink. A few drops of the extracts, evaporated to the consistency of syrup, poured into water, suffice to immediately convert the latter into ink.

Ink powders.—These are pulverulent preparations which, when dissolved in water, convert the latter into ink. By skillful manipulation, almost all inks can be reduced to powder.

Ink powder containing gallotannic and gallic acids.— To prepare this ink powder, proceed as follows : Exhaust the nut-galls, either fresh or previously moulded, as required for the formation of gallic acid, by boiling with water. Take the same quantities of nut-galls given in the directions for preparing inks containing gallotannic or gallic acid as well as the prescribed quantities of water, but it is best to divide the latter in several portions, so as to sufficiently extract the nut-galls.

The filtered clear extracts are combined and carefully evaporated in a shallow porcelain dish. When the mass has acquired the consistency of syrup, commence stirring

and continue to do so until the residue in the dish is entirely dry. To prevent scorching of the nut-gall extract, the temperature should be as low as possible.

The ferrous sulphate, previously thoroughly dried, is converted into a fine powder and intimately mixed with the pulverized gum-arabic, the mixture being ultimately combined by trituration with the powdered nut-gall extract. The resulting brownish mass being hygroscopic is at once brought into bottles, which should be well stoppered. A very small quantity of this powder thrown into water yields a very good ink.

Logwood chrome ink powder is obtained by carefully evaporating to dryness logwood chrome ink, or, in a still more simple manner, by finely pulverizing thoroughlydried logwood extract and triturating it with finely-pulverized chromate of potassium.

Ink powders possess the property of absorbing moisture from the air, and are, therefore, best kept in bottles with well-fitting stoppers, or in well-closed packages. Though the powder does not suffer, as regards quality, but, by absorbing moisture from the air, it is converted into a viscous mass, difficult to remove from the package containing it.

A very cheap method of preparing receptacles for keeping ink powder so as to be entirely protected from moisture is as follows: Melt paraffin and heat it to about the temperature of boiling water. Then by means of a spoon fill the pasteboard boxes intended for the reception of the ink powder, as well as the lids belonging to them, with the melted paraffin and immediately pour it out again. The pasteboard is rendered perfectly airtight by the thin coating of paraffin formed, and the

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ink powder put into boxes thus treated keeps perfectly dry, even when stored in a damp place.

The principal requisites in preparing ink powder are that the evaporation of the extracts and the subsequent drying be effected at as low a temperature as possible, in order to avoid scorching, and that the constituents are intimately mixed, which can only be effected by continuous trituration in the mortar.

A few formulæ for preparing ink powders are here given :---

Frick's ink powder.—Pulverized nut-galls 42, ferrous sulphate 30, gum-arabic 15, alum 6.

The nut-galls, together with the alum, are finely powdered and mixed with the other ingredients, previously thoroughly dried and pulverized. The powder is packed in boxes.

A small quantity of this powder thrown into water yields, in a short time, a fairly good ink, which, however, forms a thick sediment, from which it must be poured off. An ink powder completely soluble may, however, be readily prepared by extracting the nut-galls by themselves with water, evaporating the extract to dryness, and mixing the residue with the other ingredients.

The only object of the large quantity of alum prescribed in the formula is to prevent the moulding of the nut-gall extract. The same purpose is attained by substituting for the alum a very small quantity—about  $\frac{1}{1000}$  of the weight of the entire mass—of salicylic or boric acid.

Very fine ink powder.—Nut-gall extract 150, ferrous sulphate 25, cupric sulphate (blue vitriol) 5, alum 10, gum-arabic 10.

These ingredients, thoroughly dried and mixed, immediately yield, when brought into water, a beautiful black ink of excellent quality.

Logwood ink powder.—Logwood extract 500, chromate of potassium 1.

Pour sufficient water upon the logwood extract in a pot that the whole on heating is converted into a thick fluid, and then add the chromate of potassium dissolved in a small quantity of water. Then, with constant stirring, evaporate the mass to dryness, then dry it thoroughly, pulverize it, and bring it, while still warm, into boxes.

Alizarin ink powder.—Tannic acid 450 parts, crystallized sulphate of iron 350, chloride of sodium 250, bisulphate of potassium 75, dry indigo-carmine 50, pieric acid 4.

Mix the sulphate of iron (reduced to a coarse powder) and chloride of sodium, and dry them in an iron pan over a naked fire, constantly stirring. Lastly, reduce the mass to a fine powder. Rub the bisulphate of potassium to a fine powder in a mortar, and mix this intimately with the picric acid. Then mix this mass with that first prepared, and lastly incorporate the other ingredients. (Picric acid is poisonous, and under certain conditions explosive. It should be manipulated as directed above.) The resulting product is a green powder, which, when dissolved in 15 parts of water, yields a superior ink, which turns jet black.

Document ink extract.—Tannic acid 50 parts, tersulphate of iron (dry) 20, dry sulphate of sodium 10, sugar 20, aniline blue, water-soluble, IB., 4.

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Reduce the ingredients to a coarse powder and keep it in a tin box.

For use, pour the contents of the box into an earthen jar, add 1 quart of pure hot water, and stir until everything is dissolved. When cold, the ink is transferred to bottles. This ink writes with a bluish color, and turns rapidly black.

The dry tersulphate of iron, for the present purpose, is best prepared by evaporating 250 parts of *liquor ferri tersulphatis*, U. S. P., on a water-bath to a syrupy condition, then adding the dry sulphate of sodium, and transferring the mass, in thin layers, upon plates of glass, which are to be placed in a drying closet until the mass is dry, when it may be reduced to powder.

Ink tablets.—These are coherent masses which, when dissolved in water, yield ink. Inks consisting of a dark-colored solution, like chrome ink, are most suitable for the preparation of ink tablets; chestnut ink is also quite adapted for the purpose.

Ink tablets are prepared by pouring ink evaporated to the proper concentration into moulds or into a flatbottomed dish, and, after cooling, cutting the mass in square pieces of suitable size, which may be wrapped in tin-foil or enclosed in boxes.

The proper consistency of the mass is recognized by allowing a drop of it to fall upon a metal plate; if the drop immediately congeals to a doughy mass, the forming of the tablets may be commenced with. Ink tablets have the advantage that indigo-carmine may be used in their composition, which cannot be well done with ink powders, on account of the doughy constitution of the indigo-carmine.

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Chromium ink tablets.—I. Logwood extract 500, chromate of potassium 1, alum 10, gum-arabic 20.

The ink tablets prepared according to the above formula yield violet ink. Use as little water as possible—only sufficient to allow of an intimate mixture of the ingredients.

II. Logwood extract 100, chromate of potassium 1, gum-arabic 10, indigo-carmine 5.

These ink tablets yield an ink at first blue, but soon becoming black.

Chestnut (æsculia) ink tablets.—Extract of horse-chestnut shells 100, ferrous sulphate 10, alum 2, gum-arabic . 5, indigo-carmine 5.

The extract is prepared by boiling the green shells of horse-chestnuts or the young branches, and evaporating the decoction until it has acquired a doughy consistency.

## XVI.

### PRESERVING AGENTS FOR INK.

THE formation of mould was formerly considered a disagreeable but unavoidable accompaniment of ink. However, the formation of mould upon the surface of the ink is preceded by several phenomena injurious to the quality of the ink.

Some inks, especially those which, instead of gumarabic, contain more or less sugar, in order to impart to them a certain lustre, become viscous, so that in a short time they draw long threads on the pen, and writing with them becomes impossible. The cause of this phenomenon

is a peculiar fermentation of sugar, called mucic fermentation.

Such viscidity may be removed by adding to the ink freshly-prepared nut-gall extract, and shaking in a capacious bottle. A black, viscous precipitate is, after sometime, formed, but the supernatant fluid is a useful ink.

Of still greater injury to the ink are the fermenting processes by which lactic acid is formed, and the tinctorial matter of the ink is gradually destroyed. If an ink shows an intense acid taste—which is due to the presence of lactic acid—and constantly becomes paler, it is an indication that it will in a short time become entirely useless. Such ink may, however, be saved by the addition of bright iron—for instance, by boiling it with a few iron nails, whereby the ferment is killed and the lactic acid present fixed.

The phenomenon of decomposition appearing most frequently in inks is the formation of mould. The ink thereby becomes covered with a thick, felt-like coat of a gray-green color, which, no matter how often it may be removed, is constantly renewed, and with such rapidity that in the course of one night the entire surface of the ink is coated with mould.

This disagreeable phenomenon may be counteracted by throwing away the ink contained in the inkstand and boiling the latter in water, whereby any adhering moulds are killed. However, this affords only momentary relief, for when fresh ink is brought into the inkstand, and remains only for a short time in contact with air, the formation of mould recommences, which soon covers the entire surface.

However, in modern times, agents have been found which entirely prevent the formation of mould. The use of a larger quantity of ferrous sulphate than that actually required for the formation of the blackeolored combination with the tannin has a preserving effect upon the ink; but, besides expense, this excess of ferrous sulphate is in so far injurious that a thick sediment is gradually formed in the ink, and its color beeomes paler.

An addition of alum, which is also inimical to the development of mould, has given good results, but is accompanied by several disadvantages. Alum is an expensive product, and possesses acid properties, in consequence of which it attacks steel-pens quite vigorously. Now, if the ink contains certain organic coloring substances in solution, and is not quite acid, combinations of the tinetorial matter with the alumina are in the course of time separated, which impair the fluidity of the ink and at the same time make it paler. This may be plainly observed in inks which, besides logwood extract, also contain alum.

It has also been observed that alizarin inks, prepared with ordinary vinegar, are subject to the formation of mould, while those prepared with wood-vinegar are entirely free from that defect. The reason for this is that crude wood-vinegar always contains a small quantity of carbolic acid, which is one of the best preservatives of ink known. Hence, instead of using crude wood-vinegar, it is recommended to add to the ink a very small quantity of carbolic acid. It occurs in commerce in a white crystalline mass at a very low price.

However, the disagreeable odor of carbolic acid, which is still very pronounced even in strong dilutions, is objectionable, and some inks, otherwise excellent, cannot be sold on that account.

Crystallized salicylic acid, which is entirely odorless and harmless, may be highly recommended as an excellent preservative for ink, 6 to 12 drachms of it being sufficient for the preservation of 100 quarts of ink. It may be added to the ink in a solid state, or dissolved in a small quantity of alcohol.

Boric acid also is a good preservative. It occurs in commerce in transparent, colorless plates, soluble in about 25 parts of cold water, and in a much smaller quantity at the boiling heat. For the preservation of ink the most convenient way is to suspend a small linen bag, containing the necessary quantity of acid—for instance,  $3\frac{1}{2}$  ozs. of it for 100 quarts of ink—in the latter, and allow it gradually to dissolve.

Corrosive sublimate (mercuric chloride), proposed by some as a preservative for ink, cannot be recommended, it being, on the one hand, rather expensive, and, on the other, poisonous, and besides, as a preservative, is far surpassed by salicylic acid.

Volatile oils, especially oil of cloves, also possess preserving properties, and for this reason the addition of a few drops of oil of cloves or of a few cloves to the ink, is recommended in some formulæ.

Ink preserved with the assistance of this volatile oil possesses the characteristic odor of it, which is not agreeable to many persons. Besides, if the ink stands for sometime in the air, the oil loses its preserving power by becoming resinous.

In reviewing the preserving agents for ink mentioned above, it is evident that the use of salicylic and boric acids offers the greatest advantages.

# XVII.

## CHANGE IN THE COLOR OF INK IN OLD DOCU-MENTS AND METHODS OF MAKING FADED WRITING LEGIBLE.

THE preserving agents for inks, mentioned in the preceding section, having been in use for a comparatively short time only, no final conclusion regarding the behavior of writing executed with such inks can be arrived at, and, hence, only a description of the older kinds of ink, which were exclusively ferro-tannate inks, can here be given.

The writing of documents, though executed several centuries ago, may and does frequently show a beautiful black color, if kept in a dry room entirely free from mould.

However, these two factors rarely occur together. It is very difficult to entirely exclude all moisture, and hence the best-preserved documents show, when examined with the microscope, germs of mould, which, if the paper or parchment were exposed to a somewhat greater degree of moisture, would develop and soon destroy the writing.

In the destruction of writing by the action of moisture or mould, or of both together, the black color gradually disappears, and is replaced by a brown, which finally passes into a pure rust-color. The ink is then entirely destroyed, the rust-colored writing consisting only of an iron salt (basic ferric sulphate). By soaking the paper in water, and several times repeating the operation, the rust-colored writing constantly becomes paler, and finally entirely illegible.

Great care must be exercised when attempting to restore the faded writing of old documents, since, with the careless use of chemicals, it might happen that the characters, instead of being restored, are entirely destroyed.

One of the best means of making old faded writing, executed with ferrous sulphate ink, legible is to convert the iron salt adhering to the paper into ferrous sulphide. The latter having a black color, the writing comes out quite plainly.

However, this process is only suitable for making the writing legible without keeping it so. In a few hours, frequently already in half an hour, the writing again disappears by the oxidation of the ferrous sulphide, and its conversion into rust-colored ferric sulphate.

After many experiments the process has been successfully modified in so far that the restored writing will be preserved for at least a few days, so that if required it may be copied. For this purpose a pasteboard box about 4 inches deep and of a length and width corresponding to that of the document is used. The box is open on top and can be closed by a glass plate. At about half the depth of the box a frame is inserted, over which is stretched a net of fine white silk or cotton threads. Two porcelain saucers containing yellow ammonium hydrosulphide are placed upon the bottom of the box, and after placing the document, the writing of which is to be rendered legible, upon the net, the box is covered with the glass plate. Before placing the document upon the net, pass over it a sponge dipped in distilled water, so that the paper appears thoroughly moistened without being soaked through. Especially if both sides of the document are covered with writing, the moistening must not be carried too far, otherwise the characters soak through, *i. e.*, become visible on both sides of the paper.

The yellow ammonium hydrosulphide may be obtained in any drug store, or prepared by saturating a solution of ammonium with well-washed sulphuretted hydrogen gas evolved from ferrous sulphide and sulphuric acid, until no more of the gas is absorbed. The solution is nearly colorless at first, but becomes yellow after a time, without, however, suffering material injury, unless it has been exposed to the air.

After having for a short time been exposed to the action of the vapors of the ammonium hydrosulphide, the writing acquires at first a brown, and then a black, color. By allowing the document to remain in the closed box, the dark color is preserved, the oxidation of the ferrous sulphide being prevented by the presence of the ammonium hydrosulphide vapor, and the writing may be copied at leisure.

In many cases the writing may also be permanently restored by the following process :—

Dip the document in a fluid obtained by mixing 1 part by weight of chemically pure hydrochloric acid with 100 of distilled water. It is only necessary to immerse the document for a moment, so that the surface of the paper becomes moist. The hydrochloric acid used must, however, be absolutely free from iron.

After almost entirely drying the moistened paper in the air, scatter over it, by means of a sand box, a uniform

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layer of finely-pulverized yellow prussiate of potash and cover it with a glass plate lightly loaded down. After a few hours take off the glass plate, dry the paper entirely, and remove the yellow prussiate of potash with a fine brush.

If the paper, when scattering upon it the yellow prussiate of potash, possessed the proper degree of moisture, the writing will appear with a beautiful blue color. This is due to the fact that by the action of the yellow prussiate of potash upon the iron salt, which has been slightly dissolved by the hydrochloric acid, a combination of a blue color—the so-called Berlin or Prussian blue—has been formed.

The hydrochloric acid adhering to the paper must be removed by careful washing, otherwise, even if present only in very small quantity, it would destroy the paper. For this purpose, float the paper for 24 hours upon a solution of 2 parts by weight of crystallized soda in 100 of distilled water, then wash it several times with pure water, and finally dry it.

The writing restored by this method is of a bcautiful dark-blue color, and permanent if kept in a dark room. By too much exposure to the light it becomes paler.

The restoration of faded writing upon parchment is more difficult than that upon paper, the parchment, by reason of its mode of preparation, containing substances which, by the action of chemicals, are themselves converted into colored combinations.

According to Moride's method, the parchment is to be placed in distilled water until it swells up, during which operation it must not be touched. The swelled parchment is allowed to drain off, next dipped 5 seconds in a solution

of 1 part by weight of oxalic acid in 100 of distilled water, then washed with pure water, and finally brought into a solution of 1 part of gallic acid in 100 of water, in which it remains until the writing becomes legible. The parchment is then washed by repeatedly drawing it through distilled water, and finally dried as quickly as possible between blotting-paper.

The chemical process taking place thereby is as follows: The oxalic acid renders the iron salt remaining from the destroyed ink soluble, and the gallie acid forms with it a black colored combination.

However, the substance of the parchment frequently contains so much iron that by the treatment with gallic acid it acquires such a dark color as to make the writing illegible; and if the parchment is rotten by age, it rapidly turns brown when treated with gallic acid, and the writing will plainly appear only when the action of the chemicals is limited as much as possible. In such cases, more dilute solutions than given above are to be used, and, if necessary, the entire process is to be several times repeated.

The treatment with oxalic acid requires the greatest care, since, as previously mentioned, the object of its use is to form a soluble salt, and, hence, if too long exposed to its action, the iron salt would be entirely dissolved, and, instead of making the writing more legible, it would be entirely destroyed.

If the writing of a valuable document is to be restored, it is recommended to first experiment with a very small portion of it before subjecting the entire document to the action of chemicals.

Results, at least equal to those produced by the

above-described method, have been obtained by exposing old parchment to the vapors of acetie acid, then drying, and, after spreading it out upon a glass plate, pouring gallic acid over it. For this process the parchment must also be first swelled in water. Treatment with steam arising from boiling water is, however, to be preferred to swelling in water, since, by the latter treatment, the parchment frequently suffers injury.

# XVIII.

### COLORED INKS.

ALTHOUGH black inks are most commonly used for writing, the public also demands inks of another color. With our present knowledge of chemistry, it is not diffieult to prepare ink of any desired shade, and since the introduction of the aniline colors, violet or green inks may, for instance, be produced by simply dissolving the respective aniline colors. Besides these, inks of all possible shades may be obtained by the use of various chemicals. Some of these inks are quite popular and in frequent demand. It may, however, be remarked, that none of them-except genuine indigo-carmine ink-can compete, as regards durability, with the black inks, the writing executed with many of them becoming pale in the eourse of a few months. Hence, documents intended to be preserved for any length of time should be written with good black ink.

In the following pages directions for the preparation

of colored inks are given, those of one color being grouped together :---

I. RED INKS.—For the preparation of red inks, Brazil wood and cochineal are chiefly used, and in modern times also the chemical preparation known as aniline red or fuchsine. Of Brazil wood, as well as of cochineal, several qualities occur in commerce, and it being of importance to select the raw materials which yield the most beautiful coloring substances, a short description of both of them is here given.

Brazil wood.—Brazil wood is derived from Caesalpina echinata, a tree indigenous to tropical America, especially to Brazil. The fresh wood is pale red, but becomes darker red on exposure to the air.

In commerce several varieties of Brazil wood are distinguished, that known as Pernambuco (Santa Cruz) wood being the best and richest in coloring matter; next in order come the Japanese, Jamaica, Braziletto and Bahama woods.

Brazil wood contains a coloring matter—brazilin soluble in water and yielding with alum and tin-salts combinations of a beautiful crimson color, which are much used in dyeing, as well as in the preparation of ink, though the colors produced with them cannot compare with those obtained with cochineal, which is, however, far more expensive.

Cochineal.—The cochineal insect is indigenous to Mexico and Central America, and has been introduced into and is cultivated in some of the West Indian Islands, the Canaries, Algiers and Southern Spain. It feeds on different species of cactus. During the rainy season in Mexico the insects are kept under cover upon cactus

branches, and when the weather begins to be favorable they are *sown* upon the plants, and the young ones allowed to develop until the females become fecundated and enlarged, when they are brushed from the branches, killed by dipping them into hot water and afterward dried in the sun or near a fire. This process yields the black cochineal, while the silver-gray is obtained by killing and drying the insects by exposure to the hot sun or in suitable ovens. Some females are left upon the plants, and in this way three harvests are made before the rainy season again sets in.

Commercial cochineal is about  $\frac{1}{5}$  inch long, nearly hemispherical, somewhat oblong and angular in outline, convex above, flat or concave on the lower side, transversely wrinkled, readily pulverizable, yielding a darkred powder of a faint odor and slightly bitterish taste. Immersed in water, it imparts to it a red color, and swells up so that the ringed structure of the insect can be readily examined. There are two varieties met with in commerce—the *silver-gray* and the *black*. The former is of a purplish-gray, the latter of a purplish-black color; it differs from the former in the absence of the white wool from the furrows between the rings, which imparts to the other kind the gray color. Gray cochineal, when pure, contains a larger amount of coloring matter than the black variety, but has been often found adulterated : hence the latter was more esteemed, but is now also adulterated.

A simple test as to the quality of cochineal consists in rubbing it to a powder and pouring some aqua ammonia over it; pure cochineal immediately yields a carminecolored solution. Before the introduction of aniline colors, inks prepared with the assistance of the coloring matter contained in cochineal were the most beautiful; however, at present those prepared with aniline colors favorably compare with them.

Brazil-wood inks—Red Brazilin ink.—Pernambuco wood 280, tin-salt (hydrated chloride of tin) 10, gumarabic 20, water 3500.

Convert the Pernambuco wood to fine shavings, bring them into a pot together with the water, and boil thoroughly for one hour. Strain the red-colored fluid. In the meanwhile, dissolve the tin-salt in a small quantity of water; if the solution is turbid, which is due to the presence of a so-called basic salt, add a few drops of hydrochloric acid and boil, whereby it will soon become clear.

Dissolve the gum-arabic in the clear Pernambucowood decoction, and then add the tin-salt solution. The ink is now ready, and, if necessary, is evaporated until writing executed with it shows the desired sad red color.

The tin-salt forms with the coloring matter a beautiful red combination—a so-called lake—which is dissolved in the fluid. By using an excess of tin-salt, a portion of this lake separates in the form of a flocculent mass of a beautiful red color.

Pernambuco ink.—Pernambuco wood 80, alum 20, gum-arabic 20, water 600.

Like tin-salt, alum forms with the coloring matter of Brazil wood a lake of a beautiful red color. The mode of preparing this ink differs but little from that of the preceding. Prepare a decoction of the Pernambuco wood, strain it, and heat it to boiling. Introduce into the boiling hot fluid the finely-pulverized alum, together with the gum-arabic. The ink thus prepared frequently shows a violet tinge, which is remedied by gradually adding to the boiling ink small portions of finely-pulverized tartaric acid until the desired color appears. After each addition of tartaric acid, allow the ink to boil up for a few minutes, stir thoroughly, and take a sample.

Brazilin extract ink.—Brazil-wood extract 15, alum 2, tin-salt 2, tartaric acid 2, water 120.

Brazil-wood extract is found in commerce in solid masses. By dissolving it in water a beautiful red solution is obtained, which, like freshly-prepared Brazilwood decoction, can immediately be used for the preparation of ink. The use of the extract possesses the advantage that the preparation of the ink causes but little labor, and the solution can at once be made of such concentration that the evaporation of the finished ink is no longer necessary.

The inks prepared from Brazil wood, or its extract, are quite handsome, but cannot compare in this respect with cochineal or carmine inks, and in modern times they have been almost entirely superseded by aniline red inks.

Cochineal or carmine inks.—Although very beautiful ink of a fiery color may be directly prepared from cochineal, the finest product is obtained with the use of carmine, and the extra labor spent on the preparation of the latter is amply repaid by the quality of the resulting ink.

Preparation of carmine.—Convert silver-gray cochineal into a delicate powder and boil it with water for three hours. The resulting red fluid, while still hot, is very rapidly filtered through a thick linen cloth into another

kettle, heated to boiling, and then mixed with certain substances which form the actual lake.

There are numerous receipts for the preparation of carmine, but many of them cannot be recommended because the resulting product does not show a *fiery* color. It is best to use tin-salt and alum at the same time, and, if necessary, to make the color more fiery by carefully adding, drop by drop, a very small quantity of hydrochloric acid. The alum used must be absolutely free from iron, it being otherwise impossible to obtain carmine of a beautiful color. Use the substances in the following proportions :—

Cochineal 10, water 250, alum 1, tin-salt 1.

Add the alum and tin-salt to the boiling decoction, and continue boiling until all is dissolved. Then pour the clear fluid into a shallow porcelain dish, cover it with a glass plate, and let it stand in a light sunny place for a few weeks. During this time the at first dark red fluid becomes almost discolored, a beautiful red powder—the carmine—being deposited partially on the bottom of the dish and partially on the surface of the fluid. The carmine is separated from the fluid by filtering, and carefully dried between blotting-paper.

In order to obtain beautiful and very fiery carmine it is absolutely necessary to expose the dish or dishes containing the fluid to the sun; hence, during the season of the year when dull days prevail, it is impossible to obtain a beautiful, fiery product.

To obtain absolutely pure carmine, pour over the product first obtained aqua ammoniæ, whereby a beautiful red solution is formed, which is filtered and mixed with

acctic acid, whereby absolutely pure carmine in the form of a scarlet powder is precipitated.

To prepare from pure carmine the most superb red ink, it is only necessary to dissolve it, the process being as follows:—

Prime carmine ink.—Carmine 8, aqua ammoniæ 1000, gum-arabic 20.

Bring the carmine together with the aqua ammoniæ into a wide-mouthed glass bottle, which stands in a sheet-iron pot filled with water. Pour the aqua ammoniæ upon the powder, and heat the water in the pot nearly to boiling, keeping the fluid at this temperature for about ten minutes. The solution thus formed is, immediately after cooling, filled in bottles, which are to be closed by well-fitting corks.

It will be observed that when using this ink, and especially when the bottle containing it has for sometime been opened, the color becomes paler, and a scarlet sediment is formed. This is due to the fact that the solvent—the aqua ammoniæ—evaporates, and the carmine, which is insoluble in water, separates. To bring the carmine again into solution, it is only necessary to add to such ink a few drops of aqua ammoniæ and shake.

The solution prepared according to the following directions is brought into commerce under the name of *soluble carmine* or *carmine solution*. It is much used for painting in water-colors.

Commercial aqua ammoniæ is not always of the same strength; however, the effect of an excess of aqua ammoniæ is that the solution of the carmine acquires a purple or violet shade of color. Hence, it is best not to add the entire quantity of ammonia at once, but gradually. If the solution should, nevertheless, show a too violet shade of color, very carefully add hydrochloric or acetic acid until the color changes to the beautiful scarlet, which distinguishes carmine.

Superfine cochineal ink.—Cochineal 20, ammonium carbonate 1, alum 1, water 100.

Dissolve first the ammonium carbonate found in commerce in colorless crystals, in water at the ordinary temperature, pour the solution into a large glass bottle containing the finely-pulverized cochineal and alum, and thoroughly shake every quarter of an hour. In three to four hours all the coloring matter is extracted, and the ink filtered off.

The addition of alum to this ink is necessary for the purpose of precipitating a number of substances, which, besides the red coloring matter, are extracted from the cochineal, and for preserving the ink. If the addition of alum be omitted, the ink readily becomes viscous, and in a short time putrefies, evolving such a disagreeable odor that, though it can still be used, many persons prefer to throw it away.

Indelible silica carmine ink.—This ink is prepared by triturating carmine in a porcelain mortar with solution of water-glass until a homogeneous thick paste is formed. To this paste, water-glass solution is added, with constant trituration until the ink has acquaired the requisite color and fluidity. The ink is to be immediately filled in bottles, to be closed with well-fitting corks, and for use only a few drops—as much as required for writing—should be poured out. This precaution is necessary, since water-glass possesses the property of being

converted, on exposure to the air, first into a jelly-like, and later on, into a glassy mass, the silica being separated.

Independent of its beautiful, permanent lustre, this ink is distinguished by its great power of resistance. By using the water-glass solution as little concentrated as possible, the ink penctrates deeply into the paper, and can only be removed by caustic alkalies, though, even then, the characters will not be entirely destroyed.

Odorless carmine ink.—Cochineal 40, crystallized soda 80, cream of tartar 250, alum 20, gum-arabic 40, water 900, alcohol 50, or salicylic acid 1.

The ink is prepared as follows :----

Reduce the cochineal to a fine powder, dissolve the soda in the water, and stir the pulverized cochineal into the solution. Let the latter stand a few days, stirring it frequently. The entire mass is then heated to boiling, and the pulverized alum and cream of tartar are brought into the boiling fluid. The latter thereby foams up, and hence a capacious vessel has to be used and the powder introduced in portions. After boiling for half an hour, strain the fluid and again boil the residue with 100 parts of water. The gum-arabic is dissolved in the fluid immediately before straining.

The addition of alcohol is required to preserve the ink, it being very liable to decompose; however, an addition of salicylic acid is more suitable. Dissolve the salicylic acid in as little hot water as possible, pour the solution into the finished ink, and stir.

By the addition of salicylic acid a permanent and odorless ink is obtained. Since it is entirely free from injurious metallic salts, it may also be used for coloring candies, etc., red.

Red patent ink.—Cochineal 10, tin-salt 2, sal-ammoniac (chloride of ammonium) 2, water 200.

Boil the cochineal with the water until all the coloring matter is extracted, mix the warm fluid with aqua ammoniæ, and filter. To the hot filtrate add first the salammoniac and then the tin-salt.

Cheap cochineal ink.—Pernambuco wood 60, tartar 15, alum 15, gum-arabic 15, water 500, cochineal 5, spirit of wine 60.

First boil the Pernambuco wood with water for  $1\frac{1}{2}$  hours, then add the tartar and alum, again boil  $1\frac{1}{2}$  hours, dissolve the gum-arabic in the fluid, and mix the ink with the alcoholic extract of cochineal, prepared by pouring strong spirit of wine over the pulverized cochineal and letting stand for eight days.

By again treating the boiled Pernambuco wood and the cochineal with one-fourth of the other substances, an ink is obtained which may be combined with the first.

Purple ink.—Logwood extract 15, crystallized verdigris 10, alum 50, gum-arabic 30, water 800.

Dissolve the logwood extract by itself in water and add to the solutions the boiling hot solutions of the verdigris and alum and of the gum-arabic. If the color of the fluid should be too much inclined towards blue, add drop by drop strong vinegar or a quantity of dark red (carmine) ink.

*Carmine purple ink.*—This is prepared by adding to a good quality of carmine ink some indigo-carmine solution,

whereby the scarlet color of the carmine is changed to a pure purple or violet.

Purple carthamin ink.—Safflower carmine (carthamin) 7 ozs., gum-arabic 26 ozs., cream of tartar 1 oz., sugar  $2\frac{1}{2}$  ozs., water 6 quarts, carbolic acid  $2\frac{1}{2}$  drachms.

Red fuchsine ink.—Fuchsine is much used in dyeing, and is a very suitable material for the preparation of excellent red ink. In commerce it is found in the form of crystals, exhibiting a beetle-green lustre and yielding with alcohol a dark-red solution.

The ink is best prepared according to the following directions :---

Fuchsine 2, gum-arabic 5, alcohol 10, water 100.

Pour the alcohol (90 per cent.) over the finely-rubbed fuchsine and effect complete solution by gentle heating. Dissolve the gum-arabic by itself in the water, strain the solution, and heat to boiling. Into the boiling solution pour the fuchsine solution in a thin jet, stirring constantly.

Aniline inks in general.—Besides aniline red or fuchsine, there are numerous aniline combinations of various colors, blue, green, violet, yellow, brown, etc., which may be used for the preparation of differently-colored inks. The solution of the coloring matter is effected in the same manner as given for fuchsine.

By the introduction of water-soluble aniline colors, the preparation of these inks has been much simplified. Dissolve the coloring matter in sufficient water that a sample of the solution yields writing of a handsome color. The solution, however, should not be of such concentration that the writing, when dry, shows a metallic lustre. Mix the solution with a sufficient quantity of gum-arabic solution—and for copying inks also with glycerin—to give the ink the required degree of fluidity.

The comparatively high price of aniline colors need not to be taken into consideration, since, nevertheless, very cheap inks can be prepared with them, they yielding more coloring matter than any other dye-stuff.

Aniline inks are distinguished by a very pure, bright color, and may be advantageously used instead of watercolors for coloring photographs, steel engravings, etc.

II. BLUE INKS.—Besides water-soluble aniline blue, a solution of indigo-carmine in water deserves special consideration, it yielding an intense color and penetrating deeply into the paper, so that the writing cannot be readily removed by washing.

Indigo blue ink.—Indigo-carmine 10, gum-arabic 5, water 50 to 100.

Dissolve in the water first the gum-arabic, then the indigo-carmine, and dilute the solution with sufficient water that it will yield writing of a beautiful blue color.

Berlin blue ink.—The Berlin or Prussian blue found in commerce is an insoluble substance which may be used for the preparation of ink, but does not yield as good a product as the so-called "soluble Berlin blue."

Soluble blue is also much used for laundry purposes. It is prepared as follows :—

Preparation of soluble Berlin or Prussian blue.—Mix in a glass flask 10 parts by weight of crude hydrochloric acid with 1 of nitric acid, dilute the fluid with 10 parts of rain-water, and pour it over pieces of old iron in a porcelain or stoneware pot. After a few days pour off the clear solution of ferric chloride formed and filter it through blotting-paper.

At the same time dissolve 10 parts of yellow prussiate of potash in 100 of rain-water, and gradually mix the solution of ferric chloride with that of the yellow prussiate of potash, whereby a beautiful blue precipitate is formed, which rapidly settles on the bottom of the vessel. The supernatant fluid is then tested, first with a small quantity of iron solution; if a precipitate is again formed in the clear fluid, too little ferric chloride solution is present; if, on the other hand, no precipitate is formed by the iron solution, but by the addition of yellow prussiate of potash solution, too little yellow prussiate of potash is present.

In both cases gradually add very small portions of one or the other solution until a perceptible precipitate is no longer formed. The clear supernatant fluid is then drawn off, and the precipitate several times washed with clean rain-water. Finally, the blue precipitate is brought upon a filter and allowed to dry to a doughy mass. This doughy mass is then triturated in a large porcelain mortar with  $\frac{1}{10}$  of its weight of crystallized oxalic acid, water being gradually added, whereby a beantiful sky-blue solution of Berlin blue is formed, which can immediately be used for the preparation of the ink.

To save the labor of preparing the iron solution by means of hydrochloric and nitric acids, ferrous sulphate (green vitriol) may be used for the preparation of Berlin blue. Dissolve the ferrous sulphate in water, add to the solution one-tenth of the weight of ferrous sulphate used of nitric acid and set the acidulated fluid aside for a few days for the ferrous oxide to be converted into ferric oxide.

The preparation of soluble Berlin blue by means of this solution of ferrous sulphate is identical with that described above. It is of importance in both cases not to allow the Berlin blue to dry, but to treat it with oxalic acid while in a moist state.

If commercial Berlin blue is to be used, it must be subjected to a preparatory operation in order to obtain it in a soluble form. Experience has shown that ordinary, almost entirely dry Berlin blue is soluble only in a very large excess of oxalic acid, and that the ink thus prepared strongly attacks the pen on account of its large content of acid.

To prepare commercial Berlin blue for solution reduce it to a very fine powder, stir it in a glass or porcelain vessel with its weight of ordinary sulphuric acid, and set the whole aside for 24 to 36 hours. Then pour the entire mass into a large vessel filled with water. After the deposition of the precipitate draw off the water, and wash the precipitate with water until a sample of the water does not show a blue color with yellow prussiate of potash solution, which indicates the entire removal of the excess of iron.

The precipitate, without being dried, is then triturated with crystallized oxalic acid and treated with water. Comparative experiments have shown that about 6 parts of Berlin blue, prepared according to one of the methods above described, completely dissolve in 1 part of oxalic acid, whilst ordinary commercial Berlin blue requires three times its weight of oxalic acid for solution.

Independent of the costliness of such solution, it is use-

less for ink, as well as for laundry purposes, because the oxalic acid not only vigorously attacks steel-pens, but it would also, in a short time, destroy the substance of the paper or of the linen.

Blue post-office ink.—I. Yellow prussiate of potash 9 drachms, water 19 ozs. II. Ferrous sulphate 9 drachms, water 55 ozs.

Mix the fluids and pour over the bluish precipitate— Nitric acid 5 drachms, hydrochloric acid 21 drachms,

water 17 ozs.

Set the whole aside for 24 hours; then wash the precipitate, triturate it with two drachms of oxalic acid, and finally mix it with 4 quarts of water in which  $5\frac{1}{2}$  ozs. of gum-arabic have been dissolved.

Blue aniline ink.—Dissolve water-soluble aniline blue in water and dilute the solution so that writing executed with it shows, when dry, a pure blue color without metallic lustrc; then add sufficient gum-arabic solution to give the ink the required dcgree of fluidity. By an addition of glycerin the ink may be made suitable for copying.

Ink to rule faint lines.—Dissolve in a small quantity of warm water 20 parts of Berlin blue by the aid of 3 parts of yellow prussiate of potash, and dilute the solution with thin gum-water until the proper degree of color is obtained.

III. VIOLET INKS.—Violet inks have already been described in the preceding sections of this work, but they may also be prepared in another manner. Violet belongs to the so-called compound colors, which are produced by mixing two other colors, so that a violet fluid may be produced by mixing a red and blue fluid. The directions for violet ink previously given have the advantage of yielding very cheap products, but they do not possess the sad actually violet-blue color of aniline violet inks.

Violet aniline color ink.—The process of preparing this beautiful ink is nearly the same as that given for red fuchsine ink. Dissolve aniline violet—the so-called methyl-violet—in alcohol. The alcoholic solution may then, without previous boiling, be diluted with the necessary quantity of water; but in adding the latter great care has to be observed. If, on adding a further quantity of water, the fluid becomes cloudy, it is a sign that aniline violet begins to separate. The addition of water must then immediately be stopped and some more alcohol added. In the fluid sufficiently diluted with water, dissolve as much gum-arabic as required to give the ink the proper degree of fluidity.

Violet aniline ink, though very beautiful as regards color and at the same time eheap, has, like all aniline inks, the disadvantage of not being very durable, and especially of being readily and completely destroyed by chemical agents.

For a durable violet ink the following composition deserves the preference :---

Violet indigo ink.—For the preparation of this ink, indigo-carmine and cochineal-carmine are used. Prepare from indigo-carmine an aqueous solution of such concentration that it may be used as a blue ink, and add to it sufficient gum-arabic to give it the proper fluidity for writing. To this blue ink gradually add a very concentrated (thickly-fluid) solution of cochinealcarmine, testing after each addition the appearance of the ink in writing. The color of the ink gradually passes through purple into violet, any desired shade of which may be produced. A more beautiful, but not so durable, violet ink is obtained by mixing soluble Berlin blue with cochineal-carmine.

Violet copying ink.—Dissolve in 800 parts by weight of water 10 of glycerin, 40 of logwood extract, 5 of oxalic acid, and 30 of alum, and add a solution of 5 parts by weight of bichromate of potassium in 100 of water. The whole is then boiled in a copper kettle, and after adding 50 parts by weight of wood-vinegar, the finished ink is filled in bottles.

IV. YELLOW INKS.—There are several ways of preparing yellow ink, the simplest being by dissolving picric acid in hot water. Picric acid is found in commerce in the form of yellow crystals. It has an intensely bitter taste, is but slightly soluble in cold water, but more freely in boiling water, and is very poisonous.

Yellow picric acid ink.—A good formula for preparing this ink is as follows :—

Crystallized picric acid 10, gum-arabic 2, water 100.

Heat the picric acid together with the gum and water (rain-water) to boiling.

Yellow gamboge ink.—Gamboge is a gum-resin obtained from Garcinia Hanburii, a medium-sized tree indigenous to Siam, Cambodia, and Cochin China. It is not soluble in water, but forms with it an emulsion. To prepare the ink proceed as follows :—

Gamboge 10, gum-arabic 5, alcohol 10, water 30.

Reduce the gamboge to a fine powder, heat it together with the alcohol, add to the mass, with constant stirring,

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the gum-arabic dissolved in a small quantity of water, and finally mix the whole with the water.

Imperial yellow ink.—French berries 280, alum 28, gum 36, water 1000.

Boil the bruised berries with the water for one hour, add the finely-pulverized alum, and continue boiling for another hour. Strain the decoction, and while still hot add the gum.

V. GREEN INKS.—Green inks, in all possible shades of color, are obtained by mixing a blue with a yellow ink. It is best to mix indigo-carmine with picric acid, or soluble Berlin blue with picric acid, until a sad dark grass-green is obtained. There are, however, green inks which are not produced by mixing blue and yellow inks, a few formulæ for their preparation being as follows :—

Klaproth's green ink.—Crystallized verdigris 4, tartar 2, water 16.

Boil the verdigris and tartar with the water in a glass vessel or bright copper kettle, until a fluid of an intense green color is formed. Strain the fluid and fill it in bottles.

Green chrome ink.—By means of bichromate of potassium a green ink of a beautiful bright color and great durability may be prepared according to the following formula :—

Bichromate of potassium 10, hydrochloric acid 10, alcohol 10, gum 10, water 30.

Pour the hydrochloric acid over the finely-pulverized bichromate of potassium in a porcelain or stoneware vessel, and set aside for one hour. A bright red fluid is formed, to which add gradually the alcohol, stirring constantly with a glass rod. The fluid becomes

strongly heated, foams up, and gradually assumes a dark-green color. If the effect is too lively, add some water.

If a very capacious vessel is not used, the fluid readily flows over; it is, therefore, advisable to add the alcohol in small portions, and to wait until foaming up ceases before adding the next portion.

Then add to the green fluid pulverized crystallized soda as long as effervescence takes place, stopping the further addition of soda when a green precipitate has been formed.

Allow the fluid to stand in a covered vessel for one week, then filter it off from the separated mass of salt, and dilute it with water until it has acquired the desired color. Finally, dissolve the gum in it.

This green chrome ink penetrates deeply into the paper, and yields permanent green writing, which is very difficult to remove from paper.

Stein's green ink.—Mix indigo-carmine 1 oz., gum  $1\frac{2}{3}$  ozs., water 26 ozs., with picric acid 2 drachms, and boiling water 6 ozs.

Various formulæ for green inks.—I. Rub  $3\frac{1}{2}$  drachms of Prussian blue and 3 drachms of gamboge with 2 ozs. of mucilage, and add  $\frac{1}{2}$  pint of water.

II. A solution of recently-precipitated hydrated oxide of chromium in liquor of ammonia, diluted with a sufficient quantity of water. This produces a beautiful darkgreen liquid, perfectly anti-corrosive.

III. Dissolve 180 grains of bichromate of potassium in 1 oz. of water, add while warm  $\frac{1}{2}$  oz. of spirit of wine, then decompose the mixture with concentrated sulphuric acid until it assumes a brown color. Evaporate this fluid until its quantity is reduced to one-half, dilute it with 2 ozs. of distilled water, filter it, add  $\frac{1}{2}$  oz. of alcohol, followed by a few drops of strong sulphuric acid. It is now allowed to rest, and after a time assumes a beautiful green color. Add a small quantity of gumarabic, and it is ready for use.

# XIX.

## METALLIC INKS.

For the execution of calligraphic writing, inks are frequently used which yield characters showing a metallic color and lustre. Such inks may be prepared by two methods : Either by the use of actual metals, or of certain coloring matters, to which a metallic lustre is imparted by special treatment.

To obtain permanent metallic inks, noble metals gold and silver—have to be used, all other metals, being in the course of time oxidized, change their color.

Genuine gold and silver inks.—To prepare these inks, triturate either genuine gold or silver leaf in a porcelain mortar with some gum and water until reduced to the finest possible state of division. Then gradually add water, but not more than required for the production of a very thickly-fluid ink, otherwise the heavy metallic powders rapidly fall to the bottom. Before use, the inks have to be shaken.

For the preparation of gold ink, the use of a saturated solution of picric acid, instead of water, is recommended. A much larger quantity of water may then be added, the fluid nevertheless yielding writing of a bcautiful color and gold lustre. Considering the costliness of this ink, the addition of picric acid solution may be highly recommended.

Liquid gold for vellum.—Grind gold leaf with gumwater, add a little bichloride of mercury, and bottle.

Copper and bronze inks are obtained in the same manner as genuine gold and silver inks, by triturating copper foil or Dutch gold with gum-water until reduced to the finest possible state of division. On account of the content of copper in these inks, writing executed with them becomes dull in the course of time, and finally, if the paper is exposed to moisture, green.

Imitation gold ink is obtained from gold-bronze. It is, however, better to triturate mosaic gold (bisulphide of tin), which occurs in commerce in the form of brilliant gold-colored scales, with gamboge ink. Though the resulting ink does not possess as fine a lustre as genuine gold ink, it has the advantage over bronze inks of not changing its color.

*Imitation silver ink* is prepared by rubbing tin-foil with gum-water.

Colored inks with metallic lustre.—With the use of the previously-mentioned aniline inks, all possible colors with a metallic lustre may be obtained.

Writing executed with a fluid prepared by triturating the solution of an aniline color with the necessary quantity of gum for thickening and genuine or imitation silver powder, possesses the color of the respective aniline preparation, but with a metallic lustre.

For yellow, red, and brown, it is best to use gold or a gold-yellow alloy. By writing with a very concen-

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trated alcoholic solution of fuchsine, dark-red characters are obtained, which, when viewed from a certain direction, exhibit the gold-green lustre of crystallized fuchsine.

# XX.

# SOLID INKS (INDIA OR CHINESE INK).

THE Chinese, Japanese, and other nations of Asia use a peculiar kind of ink, a small quantity of which they rub with water, and in writing with it use a brush. This ink is known as *India* or *Chinese* ink. It is distinguished by its durability, permanency of color, and beautiful instre, and, on account of these valuable properties, it is preferred, for instance, by architects and enginecrs, for the execution of drawings which are to be durable. While genuine India or Chinese ink possesses these valuable properties, the color of the majority of the Enropean product is not pure black, but brownish, especially when much diluted.

The method of fabrication used by the Chinese in the manufacture of their ink is not accurately known. According to the reports of some travelers, the raw material—finely-divided carbon—is obtained by burning certain plants with a limited access of air, conducting the smoke through long tubes of paper and collecting the soot deposited in the portion of the tubes furthest from the fireplace—hence the finest product, which is used in the manufacture of ink.

According to other reports, the deposit of soot yielded by the smoke of oil of scsamum burning in lamps, fur-

nishes the material for the ink. The precise nature of the cement or mucilage used by the Chinese for cementing together the finely-divided carbon is not known. The peculiar odor of the genuine ink is very likely due to an admixture of musk.

The first requirement for the preparation of India ink is very finely-divided carbon, which may be produced as follows :—

Burn a fuel very rich in carbon, for instance, petroleum or purified oil of turpentine, in lamps with but little draught, which consequently smoke very much. The smoke is conducted through a slightly ascending zinc tube of considerable length—100 feet or more.

While the soot deposited nearest to the lamp may advantageously be used for less fine colors, for instance, for printing ink, that deposited in the more remote parts of the tube is, on account of its fine division and purity, especially suitable for the manufacture of India ink. But even this soot is not entirely pure, it containing certain tar-products, which make it appear somewhat smeary and also cause the brown color.

To purify the soot and entirely free it from these constituents, proceed as follows: Collect the finest portions of the soot and in a capacious porcelain dish stir them with sufficient nitric acid to form a thick paste. For stirring, a porcelain or glass spatula is to be used. Dilute the paste thus formed with rain-water to the consistency of honey. Then carefully heat the dish until thick acid vapors of nitric acid are evolved.

By the action of the nitric acid upon the tar-products adhering to the soot a large portion of them is entirely destroyed, finely-divided carbon being separated. Now

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dilute the mass with water, and, after allowing to settle, draw the acid fluid from the black sediment. By again pouring water upon the latter, the greater portion of adhering acid is removed. Now pour strong caustic soda lye over the washed carbon and boil for half an hour. The lye effects the complete destruction of all combinations and by several washings very finely-divided carbon, which is almost chemically pure, is obtained. Dry this carbon almost completely in a covered vessel over a fire and mix it with a perfectly clear solution of gum. Then inspissate the mass by heating so that a dough is formed, which becomes hard on cooling.

When a sample taken from the vessel shows this to be the case, take the mass from the fire and stir into it a small quantity of musk dissolved in strong spirit of wine.

To bring the finished mass into the well-known form in which India ink occurs in commerce, it has to be dried as slowly and uniformly as possible. For this purpose place the dish, carefully covered with blotting-paper to prevent the admission of dust, in a moderately-warm place until the at first thickly-fluid mass has acquired the consistency of dough and is full of cracks.

With the assistance of a broad spatula the mass is then, by kneading and pressing, shaped into a flat disk, which is allowed to dry still further until square sticks, which will plainly show the impression of a stamp, can be moulded from it by pressure.

The moulding of the sticks is effected in metal moulds engraved on the inside with Chinese characters, the picture of a dragon, etc. The mass, rolled into the shape of a cylinder, is pressed into the mould, and, after closing

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the latter, is exposed to quite a considerable pressure. The excess of the mass forced out on the edges of the mould is removed with a sharp knife. The moulded sticks are detached from the moulds by gently knocking the latter against a table, and placed upon boards to dry. Finally, the sticks, if desired, are entirely or only partially coated with gold leaf or silver leaf. Before gilding, the sticks are carefully examined as to whether they are free from cracks or fissures. If such are found they are filled up with thick ink-mass and smoothed. The sticks must be hard, show a pure black, lustrous surface and appear perfectly homogeneous and fine-grained upon the fracture.

If close attention is paid to the quality of the materials used, as well as to the moulding of India ink prepared according to the above-described process, the product cannot be recognized, even by experts, as an imitation of the Chinese article. As regards blackness and lustre of color it is not inferior, but even superior, to many of the genuine Chinese products.

In the following, several processes for the manufacture of a somewhat inferior quality of India ink than the one above described are given :—

1. Purify fine lamp-black by washing with caustic soda, dry and make into a thick paste with a weak solution of gelatine containing a few drops of musk essence, and about half as much ambergris. Mould and dry. Instead of gelatine, the following solution may be used: seed lac 1 oz., borax  $\frac{1}{4}$  oz., water 1 pint. Boil until solution is effected and make up with water to  $\frac{3}{4}$  pint.

2. For making a deep-black India ink, which will also give neutral tints in its half-shades, rub thoroughly together 8 parts lamp-black, 64 parts water and 4 parts finely-pulverized indigo. Boil the mixture until most of the water has evaporated; then add 5 parts gum-arabic, 2 parts glue and one part extract of chicory. Boil the mixture again until it has thickened to a paste, then shape it in wooden moulds which have been rubbed with olive or almond oil.

# XXI.

## LITHOGRAPHIC INKS AND CRAYONS.

LITHOGRAPHIC inks and crayons must contain substances possessing the property of offering sufficient resistance to the action of acids, and also of taking up printing ink. Such substances are wax, as well as fat and resins, when converted into soap.

Lithographic inks.—I. Wax 140, lac 100, mastic 30, pine resin 10, tallow 70, lamp-black 32.

For the preparation of this ink two copper vessels are required : a kettle provided with a lid and a pan furnished with a lip. First melt in the pan over a very moderate fire all the ingredients, with the exception of the wax, and endeavor to effect, by constant stirring, as homogeneous a mixture as possible. Then melt the wax in the kettle, and when melted continue heating. The wax soon throws up bubbles; it is decomposed and can, after a certain time, be ignited. When this point has been reached, ignite the wax and pour, with constant stirring, the mass previously melted together into the burning wax. When all has been added extinguish the

#### LITHOGRAPHIC INKS AND CRAYONS.

flame by placing the lid upon the kettle, and moderate the fire so that the mass remains in a liquid state. The homogeneity of the product is promoted by stirring.

The finished mass is poured by means of a small ladle into metallic moulds, whereby sticks resembling India ink are obtained. To write with this ink rub it with warm water, best upon a smooth porcelain plate. The rubbed ink not consumed in one day must be covered to prevent it from drying up too rapidly. By rubbing upon dried ink fresh ink, grains are frequently formed, which have a disturbing effect when working with the pen, and still more so when working with the brush.

It has also been recommended to dissolve the ink in hot water, and preserve the solution in bottles. Although this saves the labor of frequent rubbing, the latter is to be preferred, since the ink can thereby be kept more uniform and fluid.

II. Tallow 4 ozs., wax 4 ozs., soap 4 ozs., shellac 4 ozs., fine Paris black as much as required. This is an excellent ink for drawing on stone. For transfer paper the following proportions are better: Tallow 4 ozs., wax 5 ozs., soap 4 ozs., shellac 3 ozs., black about half the quantity used for stone.

The fire for ink-making should be a clear one, yet not low, as the operation requires sometime. Put into the saucepan the tallow and wax, and when melted throw in the soap, a little at a time. It must be put in in small pieces, and time be allowed for each piece to part with its water, which may be known by the cessation of the ebullition which follows. When the soap is dissolved in the wax and tallow, the heat must be continued until the dense light-colored fumes passing off can be ignited

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upon the application of a light. If the flame is two to three inches high the saucepan may be removed from the fire, when the burning will probably be continued without further application of heat to the bottom. Stirring with a rod will facilitate the passing off of the vapor. It must be burned until the 12 ozs. are nearly reduced to 8 ozs. Then put out the flame and add the shellac, a little at a time, taking care that it does not boil over. Add the black. Ink that is not sufficiently burnt becomes thick and shiny after standing for two or three hours after mixing with water. Place a grain or so on a saueer, and drop upon it a little distilled water; watch it for a few seconds, and notice whether the ink becomes lighter in color. If it does, it is a sign that the burning has been insufficient. Heat again and allow the white fumes to pass off for a few minutes without catching fire. Try the ink again. Cast it into sticks for convenient use.

Considerable difference of opinion appears to exist about the quantity of black to be used. It is variously stated at from  $\frac{1}{6}$  to  $\frac{1}{20}$  of the whole. It is better to err on the side of putting too little than too much black, because the former can be readily remedied. The black must be ground. If it be ground in turpentine and cautiously added to the ink, the heat will vaporize the turpentine. If it is added in dry powder there will be eonsiderable difficulty in diffusing it through the mass.

French lithographic ink.—Shellae 15, mastic 3, potash 3, hard tallow soap 3, lamp-black 1.

Melt the soap with the shellac and mastic; then add the potash and lamp-black, and keep the mass in a fluid state, stirring constantly. When convinced by testing a

sample that the mass is thoroughly homogeneous, cast it into sticks for use.

Vienna lithographic ink.—Wax 18, soap 18, shellac 14, pine resin 6, tallow 10, caoutchouc 2, oil of turpentine 5, lamp-black 6.

Mix the wax, soap, shellae, resin, and tallow, and heat the mass until it commences to throw up bubbles; then stir in the solution of the caoutchouc in the oil of turpentine and the lamp-black.

The mass is melted and stirred until the odor of oil of turpentine has almost disappeared, and is then cast into sticks.

Munich lithographic ink.—Wax 20, tallow 10, shellac 20, soap 20, soda 30, lamp-black 10.

Bring the constituents into a pot or a saucepan, melt and strongly heat them with constant stirring.

English lithographic ink.—Wax 6, tallow 6, hard tallow soap 6, shellac 12, mastic 8, Venice turpentine 1, lamp-black 11.

Reduce the mastic and shellac to fine powders, and gradually introduce them into the heated turpentine, then add the tallow, wax, and soap in the order named, and finally intimately combine the lamp-black with the mass by rubbing. When the mass has become somewhat more viscous by cooling, pour it into moulds or on a slab, and when cold cut it into square pieces.

Lithographic chalk.—Lithographic chalk is used for drawing upon the stonc. It must possess sufficient solidity to bear cutting to a fine point like a good leadpencil, and yield a beautiful uniform stroke, even when only gently pressed upon the stone.

London lithographic chalk.—Wax 30, tallow 25, soap 20, shellac 15, lamp-black 6.

Melt the substances and strongly heat and ignite the melted mass, allowing it to burn until it has acquired the requisite consistency. It requires some skill and experience to recognize the proper moment, which, however, can be readily acquired by extinguishing the burning mass by placing the lid upon the vessel, taking a small sample, shaping it into a stick and testing it. As long as the sample will not bear cutting to a fine point, which in writing or drawing shows a certain degree of elasticity and yields a beautiful black stroke, the mass has not the required consistency. It is again ignited and allowed to burn for a few minutes more. The finished mass is shaped by rolling upon a marble plate into sticks the size of a goose-quill, which are cut into snitable lengths.

French lithographic chalk.—Tallow 100, soap 85, shellae 70, mastic 10, lamp-black 10.

Melt the ingredients together, strongly heat the melted mass, and ignite it, allowing it to burn for sometime. Extinguish the flame by covering the vessel, and shape the mass, after it has become solid, into sticks.

Transfer or autographic inks.—The purpose of these inks is to transfer writing or drawings executed upon paper to the stone, so that the latter can, immediately after etching, be used for printing.

It cannot be denied that the preparation of autographic inks is connected with certain difficulties, since a fluid has to be produced that not only possesses the general properties of an ink, but must also bear copying after sometime in such a manner that it adheres firmly

LITHOGRAPHIC INKS AND CRAYONS.

to the stone, and the latter, after etching, furnishes a serviceable printing-plate.

For the purpose of manifolding in this manner an ordinary document, it is only necessary to execute the writing with autographic ink upon ordinary writing paper, which, however, should not be too rough. The eharacters will then be well impressed upon the stone, though a fine line may here and there appear broken.

For manifolding a calligraphie work, a pen-drawing, building-plan, etc., it is, however, absolutely necessary to especially prepare the paper, in order to obtain satisfactory impressions.

Preparation of the paper for autographic printing.— By following the directions given below, paper is obtained which, in the lithographic press, renders with perfect fidelity upon the stone the smallest dot and most delicate line, so that the plate can immediately be etched and yield many thousands of perfect impressions.

Treat fine, strong, unsized printing paper with the following mixture :--

Gelatine 10, water 100; tannin 5, water 100.

Lay the paper flat upon a plate, pour the boiled gelatinc solution upon it, and allow the excess to drain off by placing the plate in an oblique position; then pour the tannin solution upon the paper, and, after drying twice or three times, repeat the same operations—first gelatine solution, and then tannin solution. The paper is finally dried thoroughly and subjected to strong pressure between glazing rollers.

With the use of paper thus prepared, even the finest copper or steel engraving may be transferred to the stone by blacking the engraving with autographic ink,

taking an impression by means of prepared paper, and transferring the latter upon the stone.

In transferring drawings executed with autographic ink upon paper to the lithographic stone, care must be taken to several times run the stone and paper through the press with strong pressure, and then carefully draw off the paper. Repeated passing through the press is necessary, because the stone requires a certain time to take the fat-like ink so firmly that it will not be partially removed by the subsequent etching with dilute nitric acid.

Best autographic ink.—Wax 110, tallow 30, soap 110, shellac 50, mastic 40, pine resin 10, lamp-black 30.

Melt the substances in an iron vessel; then increase the temperature until fumes of a disagreeable odor are evolved, and shape the mass to cylinders, either by casting in moulds or by rolling upon a stone. For use, the cylinders are rubbed with water in a smooth porcelain dish.

This autographic ink is especially suitable for manuscripts which are to be lithographically copied. Execute the writing, in not too small characters, with a good steel-pen, and copy immediately.

Autographic drawing ink—Basis-mass.—Wax 70, tallow 75, soap 60, copal 45, shellac 70, mastic 70, pitch 10, linseed oil 10, pulverized sulphur 10.

First heat the copal with the linseed oil, and heat the mass until thick vapors of a pungent odor commence to be evolved; then introduce the other ingredients—first the soap, then the tallow and wax, and finally the resins. Now thoroughly heat the mixture and ignite it. If the flame goes down and threatens to go out, scatter

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some of the sulphur upon the mass and stir. Burning must be continued until at least three-quarters of the substances originally used are consumed. The flame is then extinguished by covering the vessel.

Autographic ink, No. 1.—Basis-mass 12, rain-water 100, indigo-carmine 5.

Boil the basis-mass with water until the fluid is reduced to about one-half; then pour off the clear, brownish fluid, dissolve in it the indigo-carmine, and fill the ink in bottles.

A basis-mass *burnt for too short a time* gives an ink which dries too much and cannot well be copied; on the other hand, a basis-mass *burnt too much* yields an ink which writes well, but does not adhere firmly to the stone. It remains to be remarked that, in transferring the writing to the stone, the back of the paper must be thoroughly moistened, the writing being thereby more readily detached.

Autographic ink, No. 2.—Wax 100, soap 30, tallow 16, shellac 8, black pitch 4, lamp-black 20.

Melt the ingredients and stir until a homogeneous mass is formed. Then heat very gradually until the mixture begins to smoke, but prevent burning by placing the lid upon the vessel as soon as the mass bursts into flame. Cast the finished ink into sticks, and for use rub it down with warm water.

Autographic colors according to Andés.—I. Shellac 3, wax 1, fat 7, mastic 4, soap 3, lamp-black 1.

II. Purified mutton suet 100, yellow wax 125, soap 16, shellac 150, mastic 125, turpentine 16, lamp-black 30.

III. Soap 100, wax 118, fat 50, mastic 50, lampblack 30.

IV. Wax 3, mutton suet  $5\frac{1}{2}$ , soap 6, shellac  $5\frac{1}{2}$ , mastic 45, Venice turpentine 1, lamp-black 10.

Copying paper.—This paper, which has obtained an excellent reputation in Germany, is, according to E. Dieterich, prepared as follows: The manufacture may be divided into two parts, viz., the production of the color and the application of the same to the paper. Dieterich uses exclusively Paris blue as covering better than any other mineral color. Ten parts by weight of the same are coarsely ground and mixed with 20 of ordinary olive oil, and finally 0.25 of glycerin is added. This mixture is for a week exposed in a drying chamber to a temperature of 104° to 122° F., and then ground as fine as possible in a paint-mill. The glycerin softens the hard paint, and tends to make it more easily diffusible.

Then melt 0.5 parts by weight of yellow wax with 7.5 parts of ligroine, and add to this 3 parts of the blue mixture, mixing slowly at a temperature of 86° to 104° F. The mass is then of the consistency of honey. It is applied to the paper with a coarse brush and afterwards evenly divided and polished with a badger's hair brush. The sheets are then dried on a table heated by steam. This is done in a few moments, and the paper is then ready for use. For black paper, aniline black is used in the same proportion. The operation must be carried on in a well-ventilated room, protected from fire, on account of the combustibility and the narcotic effects of the ligroine. The paper is used by being placed

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between two sheets of paper, the upper one receiving the original, the lower one the copy.

Another method of preparing copying sheets is as follows: Melt ten parts of purified tallow with one of yellow wax, and intimately mix the mass with 1 part of fine Paris blue. With the hot fluid uniformly coat one side of stout smooth paper. For use place the copying paper, colored side down, between two sheets of paper. By writing upon the upper sheet with a dull lead-pencil, using a certain amount of pressure, the copy of the original appears upon the lower sheet in a blue color.

# Supplement.

Copying of drawings by the photo-chemical process.— Certain chemical combinations possess the property of changing in a peculiar manner by exposure to the light, the entire process of photography being based upon this. This changeableness of certain bodies by the action of light may be utilized for the purpose of directly obtaining a true impression of a document (written upon one side of the paper only), or a drawing.

The process is called *cyanotype* or *blue print*, and is executed as follows: In a dark room saturate paper with a solution of 10 parts of ferric chloride and 5 of tartaric acid in 100 of water, and dry. *Or*, saturate the paper with a solution of 10 parts of ammonia-citrate of iron and 10 of red prussiate of potash in 60 of water.

The paper is placed underneath the drawing to be copied and exposed to the sun for one hour. A solution of ten parts of yellow prussiate of potash in 100 of water is then poured over it, and after washing and dry-

ing the paper the drawing appears white upon a blue ground.

Method of copying India ink drawings, copperplates and wood-cuts.—Dissolve oxalic acid in cold water, heat the solution to boiling and saturate it with molybdic acid. When cold, fill the fluid in black glass bottles for use. For the purpose of copying a wood-cut or copperplate also a photograph on paper—saturate paper with the above-mentioned solution in the dark, place the picture to be copied, picture side up, upon the paper and expose both under glass (in a photograph copying frame) to the direct rays of the sun. The copy appears white upon a dark-blue ground.

If the paper of the copperplate, etc., is very thick, it is rendered transparent by slightly rubbing the back with petroleum.

# XXII.

# PRINTING INK.

PRINTING ink is a very different composition from that used for writing. It is a soft, glossy compound, having a certain amount of adhesiveness, and becoming, by exposure in thin layers, perfectly hard and firm. Besides these properties, which always belong to it, it possesses other and varying attributes, according to the numerous purposes to which it is applied. Its preparation demands careful manipulation, for the presence of the smallest body in it, even if it is only a minute lump of lamp-black, is sufficient to cause a stain in printing.

One of the most valuable properties which printing ink should possess is durability, or the capacity to resist successfully the obliterating influence of time, and it should, at the same time, have brightness and depth of color. Further, printing ink should possess the property of remaining unchanged for a considerable time when exposed to the air—but must also become completely dry in a short time after it is imprinted upon paper. Finally, it must be of a consistency sufficient to prevent its penctrating so deep into the paper as to blur the appearance of printing on the other side. It onght not to affect the soft, elastic rollers which are employed to convey it to the type, and which, unless the ink be a perfectly innocuous preparation, are liable to considerable injury.

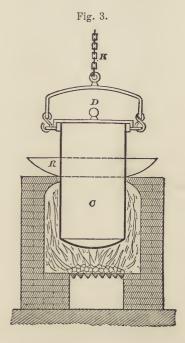
Printing ink should, moreover, have an oleaginous character; it onght to be very glossy and perfectly free from any granular appearance. If, on the extraction of a small portion from a mass, it leaves but a short thread suspended, it is considered good, but the best test of its consistency is the adhesion it shows upon pressing the finger against a quantity of it.

The ingredients of ordinary printing ink are burnt linseed oil, resin, and occasionally soap, with various coloring matters.

The linseed oil should be of the best quality, as an inferior article gives a bad smell and rusty shade of color. The oil is purified by digesting it in partially diluted sulphuric acid for some hours, at a temperature of about 212° F., allowing the impurities to subside, and then washing away the acid with repeated additions of hot water. The oil, if treated in the proper manner,

should then be of a pale-lemon color and entirely free from smell. It now dries much more rapidly than before, and must be protected from the air.

The purified oil is then partially resinified by heat. Specially constructed vessels must be used for this purpose, as the volume of the oil increases in an extraordinary degree in consequence of the many bubbles which



are formed. The most suitable apparatus used for this purpose is represented in Fig. 3. It consists of a cylinder of sheet iron, C. A rim, R, bent upwards like a shell, is placed about half-way up on the sides of the

cylinder. The top of the cylinder is surrounded by a strong iron ring, on which are fastened the chains, K, of a tackle which enables the attendants to lift the cylinder quickly from the fireplace. A helmet or cover of sheetiron, D, fitting as air-tight as possible, completes the apparatus, which should be erected in a fire-proof room. A flue connected with a well-drawing chimney is placed in the roof of the building to carry off the injurious vapors arising from the boiling linseed oil. The workman should be provided with a stool high enough to enable him conveniently to take samples out of the cylinder. The chains of the tackle are fastened to a movable crane, so that, at the word of command, an assistant can lift the cylinder immediately from the fire and move it aside. The cylinder is filled only half full with oil, a strong fire being kept under it at the commencement of the work. The oil will soon commence to bubble, making a crackling noise. This is caused by the escape of water vapors, which are developed from the oil and originate from water mechanically mixed with it. It ceases in a short time, and as the temperature rises the oil, having now become entirely black, swims quietly and uniformly in the cylinder.

From this moment on the oil rises constantly in the cylinder and throws out small bubbles wherever it comes in contact with the walls of the cylinder. As soon as vapors of a pungent odor commence to rise from the oil, the attendant must observe the strictest vigilance. The moment the entire mass of the oil commences to bubble up, and vapors are also evolved from the interior, the fire must be quickly moderated, or the fluid will surely boil over, be the vessel never so capacious. If the oil should continue rising, notwithstanding the fire having been moderated, the cylinder must at once be lifted from the hearth and only replaced when the oil has subsided.

The best plan is to keep the oil at such a temperature that the developed vapors ignite on coming in contact with a lighted candle, but will go out when the flame is removed, or can be at least easily extinguished by placing the cover upon the cylinder. The firing is then regulated in such a manner that the vapors will be developed quietly and uniformily without a further rising of the contents, and the condition of the oil is tested by the "thread-test."

To make this test, a small quantity of the oil is taken from the cylinder with a wooden spatula. This is cooled off by swinging it to and fro, and a drop of it is then squeezed between the fingers and drawn out. In doing this a viscid thread,  $1\frac{1}{2}$  to 2 inches long, before breaking, should be formed from one finger to the other. If the thread breaks before reaching that length, the boiling must be continued. If the sample is of the requisite quality, the cylinder is at once lifted from the fire and the oil allowed to cool off; or it is subjected to what is technically called "burning." This consists in igniting the vapors and allowing the oil to burn for about five minutes, when the fire is extinguished by placing the cover upon the cylinder.

Burning the oil makes it very dark. This is, of course, of no consequence when it is to be used for black printing ink, but it is best to omit the burning if the oil is to be used for colored inks; in fact, for delicate shades of color, burned oil cannot be used.

By the ebullition and ignition just noticed, the original character of the oil is totally altered. It is at first turbid, but clarifies when allowed to repose; it is now viscid and more or less adhesive; it penetrates paper with difficulty; it dries much faster than when unburnt; and it has now a pyrogenous and not unpleasant odor, which soon passes off from a thin layer exposed to the air.

Other drying oils besides linseed are occasionally used; for instance, hemp oil, being much cheaper, is sometimes substituted for linseed oil. It produces a tolerably good ink, but the disagreeable odor of the oil adheres to it, and for this reason printing ink prepared with this oil should never be used for fine colors.

The consistency of a printing ink depends upon the purpose for which it is to be used; the more elegant the printing is to be, the more the oil must be boiled down, and the greater will be the expense of producing the ink. For newspapers and, generally speaking, for matter which must be printed quickly, a more fluid ink is used than for printing books. The thickest ink is used for copperplate and lithographic printing.

Resin is an article of considerable importance in the manufacture of printing ink, since, when dissolved in the oil—after the latter has undergone ebullition and inflammation—it communicates body to the finid, and the compound bears a great resemblance to Canada balsam. For ordinary inks, the quality of the common black resin is sufficiently good, but the light-colored American resin is more suitable for colored inks. The resin should be refined by melting and filtering to prevent pebbles or plant-parts, frequently mixed with it, from getting into the ink. For 120 parts of linseed oil 40 to 50 of resin and 12 to 14 of soap are used. The purpose of adding soap is to facilitate the cleansing of the forms, which then can be accomplished by washing them with a brush. The soap to be used should be entirely dry. Yellow rosin-soap answers for ordinary printing ink, but white tallow-soap must be used for fine colors. Too much soap is apt to render the impression irregular and to prevent the ink from drying quickly. The proper proportion is when the ink works clean without clogging the surface of the types.

The coloring matters of printing ink demand great attention, as much of the beauty of the typography depends upon them.

The universal ingredient for *black* is lamp-black. There are large buildings appropriated to the sole purpose of burning oil, naphtha, spirit, etc., to produce this black, which is collected from the sides and ceilings of the chambers. Ivory-black is too heavy to be used alone as a pigment for printing ink; but it may be added, with advantage, by grinding a little of it upon a muller with the lamp-black, for certain purposes, for instance, if an engraving on wood is required to be printed so as to produce the best possible effect.

Indigo gives a deep but dull blue; it is cold, but permanent. Prussian blue needs much grinding and extra soap. It affords a deep, bright color, and is useful for making greens. Antwerp blue is easily ground to the proper degree of fineness, makes a good ink and works clean and well; its tint is bright and light, with a slight green tendency.

Various shades of green may be produced by suitable

admixture of blues and yellows. Prussian blue and chromate of lcad make a good, rich green; indigo and the same yellow, a deeper, duller color; Antwerp blue, and the same yellow, a brilliant rich green. The chromate must be quite pure to insure good colors.

For red, carmine may be readily ground into a fine ink of brilliant color by admixture with black ink varnish made with balsam of copaiba. It is expensive, but valuable for special purposes. Crimson lake is readily reduced by the muller. It works clean and does not require more soap than is contained in the varnish, but does not possess much depth. A deeper tone than can be obtained from commercial lake may be obtained in the following manner : Boil 1 oz. of the best powdered cochineal in 1 quart of water till the coloring matter is extracted. Let the cochineal subside and pour the liquid into another vessel. When cold, gradually add some chlorate of tin, with constant stirring, till the supernatant liquid on standing becomes nearly colorless; then add a little powdered alum. Assist the solution by stirring and allow to subside. Pour off the excess of liquid, wash the colored residue with three or four waters to remove the acid, and dry carefully and slowly. The addition of cream of tartar during the process will give a purple tint.

Vermilion may be used for red ink where neatness is required, as for the title-lines of books. The quantity of it employed varies much and necessitates care in its proportions. It requires much soap to make it work clean. For cheap work, such as posting bills, *red lead* may be used. It requires additional soap to make it work clean, and its color soon changes to black. An excellent permanent red of rich tone may be produced from *Indian red*. Venetian red is easily ground into a smooth ink and requires but little more soap than the varnish usually contains. It is, however, not very intense.

The highest yellow is obtained from chromate of lead, which is readily ground into a fine ink, works freely and well and requires but little soap beyond what the varnish contains. Yellow ochre is easily ground into a fine ink. It gives a useful color, dull, but permanent.

All coloring matters must be rubbed very fine and mixed with the varnish in the most careful manner, so as to obtain an absolutely uniform color.

In the manufacture of printing inks, the resin is dissolved in the burnt oil, in cast-iron pots or boilers, and the varnish thus prepared is introduced into what is termed the mixing vessel, which is cylindrical, and in the centre of which bars or rods of iron, attached to a perpendicular shaft, revolve in a horizontal position. The black or other coloring matter is then added to the hot varnish, and the whole, when thoroughly mixed, is drawn off through an opening in the base of the vessel. The pulp is next very carefully ground by being passed between hard stones of a very fine texture, driven by heavy machinery, the motive power being steam. Sometimes a second grinding is requisite, but this may generally be avoided by taking care that the varnish of resin and oil is free from gritty particles and that the black or other coloring matters are in an impalpable state.

The proportions and conditions of the various ingredients vary considerably, and great experience is required before an ink can be prepared to suit any one purpose.

#### PRINTING INK.

The oil may have to be rendered more viscid by burning in some cases than in others; sometimes the quantity or kind of resin requires to be varied, or perhaps different proportions of color are requisite. As previously mentioned, newspapers printed by steam-power require an ink of less substance than that employed for book-work. which must be tolerably stiff. For wood-cuts, the ink must not only be stiff, but very fine. The qualities of the material to which the ink is applied furnish an additional guide in this matter; thin paper must have a soft ink, which works clearly and is not too adhesive. A fine stout paper, on the other hand, will bear a stiffer and more glutinous ink; and as resin supplies these properties, so does it in a great measure communicate brilliancy, and the most perfect and splendid effects are by these means produced.

Copperplate printing inks.—Boil 1 pint of linseed oil in a dry iron saucepan until it will readily ignite by applying lighted paper. Let it burn ten minutes, and then extinguish the flame by putting the lid on the pan. Now add nearly  $\frac{1}{2}$  oz. of litharge and stir well. When cool, ready for use, mix a little of this oil with lampblack, forming a thick paste, and grind it very fine with a muller. The grinding is most important.

Black.—Frankfort black, finely ground with linseed oil, or, for very fine work, fat oil.

Red.—Mineral orange-red 5 ozs., Chinese red 2 ozs. Blue.—Celestial blue 2 ozs., marine blue 3 ozs. Green.—Mineral green 2 ozs., chrome-green 3 ozs. Brown.—Burnt umber 2 ozs., rose-pink 1 oz. Lilac.—Prussian blue 1 oz., Chinese red 2 ozs. Pink.—Mineral pink 2 ozs., satin-white 1 oz. Orange.—Orange-red 2 ozs., flake-white 1 oz. The above to be ground and mixed with Canada balsam. Or, Red, vermilion; Yellow, King's yellow; Blue, smalt; Green, King's yellow-green; Brown, burnt umber; Dark Brown, burnt umber and Frankfort black; Puce, Frankfort black and vermilion; Brown, Frankfort black and drop lake. These to be ground and mixed with nut- or linseed oil.

Gold.—Gold-bronze mixed with dark oak and mahogany varnish.

Silver, copper, ruby.—The same as for gold, merely substituting the different bronzes. Cards printed in gold, silver, or colors, should, when dry, be placed on a very smooth copper- or steelplate not engraved, and passed through a copperplate press with rather a tight pressure. This would also improve the appearance of cards printed in like manner with letter-press.

# XXIII.

## INK PENCILS OR ANILINE PENCILS.

THE materials used for the manufacture of these pencils are aniline, graphite, and kaolin in different proportions. The pencils may be used in copying, marking in permanent color, and in reproducing writing and dcsigns. In copying, a thin sheet of moistened paper is laid over the letter, design, or document, and the lines are traced with the pencil. The action of the water on the aniline gives a deep, fast tracing, resembling ink in color. On ordinary dry paper they give a mark which

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cannot be removed by India rubber. Moistened sheets of paper laid over the writing will, under a slight pressure, transfer good impressions that do not blur.

The principal conditions for obtaining a useful mass are to have the materials in the finest possible state of division, and to expose the mass to a high pressure in order to make it dense before forming it into slender sticks used in filling the pencils.

The aniline colors most suitable for the preparation of these pencils are fuchsine for red, water-soluble blue or methyl-violet for blue and violet, and nigrosine for black.

Faber's aniline pencils.—No. 1. Aniline 50, graphite 37.5, kaolin 12.5.

No. 2. Aniline 46, graphite 34, kaolin 24.

No. 3. Aniline 30, graphite 30, kaolin 40.

No. 4. Aniline 25, graphite 24, kaolin 50.

The mass is intimately mixed, made into a paste with cold water, and pressed through a screen, which divides it into slender sticks used in filling the pencils. When dry, the sticks are fitted to the wooden parts and glued together in the usual way. No. 1, of the above formulæ, gives very soft, and No. 4, very hard pencils.

New pencil as a substitute for ink.—The writing yielded by this pencil is capable of being reproduced by the copying machine. It is very black and does not fade on exposure to the light. The mass for these pencils is prepared as follows: Repeatedly boil 10 parts of best logwood in 100 of water, straining each time. The liquid is then evaporated until it amounts to 100 parts, and is then allowed to boil in a pan of stoneware or enamel. To the boiling liquid nitrate of oxide of chrome is added in small quantities until the bronzecolored precipitate, formed at first, is redissolved with a deep-blue coloration. This solution is then evaporated in a water-bath to a syrupy consistency, with which is mixed well-kneaded clay in the proportion of 1 part of clay to  $3\frac{1}{2}$  of extract. A little gum tragacanth is also added to obtain a proper consistency.

It is absolutely necessary to use the salt of chrome in the right proportion. An excess of this salt gives a disagreeable appearance to the writing, while if too little is used the black matter is not sufficiently soluble.

The other salts of chrome cannot be used in this preparation, as they would crystallize, and the writing would scale off as it dried.

The nitrate of oxide of chrome is prepared by precipitating a hot solution of chrome alum with a suitable quantity of carbonate of soda. The precipitate is washed till the filtrate is free from acid. The precipitate thus obtained is dissolved in pure nitric acid so as to leave a little still undissolved; hence the solution contains no free acid, which would give the ink a dirty-red color. Oxalic acid and caustic alkalies do not attack the writing. Dilute nitric acid reddens, but does not obliterate the characters.

*Pencils for marking linen.*—Mix 4 parts powdered pyrolusite with 16 parts of thoroughly-dried alumina. Add to this a solution of 6 parts of nitrate of silver in 10 of distilled water. Rub and knead the mass thoroughly. Pencils are formed from this and dried. Used for marking linen.

Pencils for writing on glass, porcelain, and metal.— These pencils are prepared by mixing the colors with

## INK PENCILS OR ANILINE PENCILS.

the fats in warm vessels, and grinding them to an impalpable powder. They are then allowed to cool until they have acquired the proper consistency for being transferred to hydraulic presses, in which the mass is treated and shaped similarly as the graphite in the presses for ordinary pencils.

The following formulæ for the composition of such pencils are those used at the factory of A. W. Faber, of Stein, near Nürnberg, Germany :—

I. Black.-Lamp-black 10, wax 40, tallow 10.

II. White.-Zinc-white 40, wax 20, tallow 10.

III. Pale blue.-Prussian blue 10, wax 20, tallow 10.

- IV. Dark blue.—Prussian blue 15, gum-arabic 5, tallow 10.
  - V. Red.-Cinnabar 20, wax 60, tallow 20.

VI. Yellow.—Chrome-yellow 10, wax 20, tallow 10. Pencils for writing upon glass.—I. Water 2, minium 1, tallow  $\frac{1}{4}$  to  $\frac{1}{2}$ .

Melt the ingredients together, stir thoroughly, and cast the mass into sticks. An addition of more tallow makes the mass less hard.

II. Tallow 5, wax 10, tallow-soap 10, minium 10.

Melt together the tallow, wax, and soap, and stir into the melted mass the minium; continue the stirring as long as permitted by the consistency of the mass. Shape the mass, before it entirely hardens, into sticks the thickness of a thin lead-pencil. Before use it is recommended to lay the sticks in a moderately warm place, since they become quite brittle and break readily, especially after lying for sometime.

# XXIV.

# MARKING INKS.

THE fluids known under this name are used for writing upon tissues. They must, of course, be entirely indifferent towards water, and writing executed with them must appear unchanged, even after the tissue has for weeks lain in water.

However, besides water, marking inks must also be capable of resisting the frequently very energetic action of chemicals used in washing, bleaching, and finishing tissnes, and some of them must be so durable that, after marking and dyeing the tissue, the marking should remain plainly visible, even if the coloring matter on the place where it has been executed is intentionally destroyed.

There are, comparatively, few substances which fulfil all the demands of a marking ink; only writing executed with ink consisting chiefly of carbon is absolutely indelible.

Solutions of the noble metals, gold, silver, platinum, and of iridium—which is allied to platinum—possess the property of decomposing when in contact with organic substances, so that the metal is separated in a state of very fine division, whereby the writing comes out very plainly.

The combinations of silver are already decomposed by the mere action of light, whereby they become black in consequence of the separation of very finely-divided silver. This, as well as the fact that silver is the least expensive amongst the noble metals, makes it the most suitable material for marking inks.

There are, however, also organic coloring matters which can be brought into such a form that they are absorbed by the tissue and form with it insoluble combinations; *indigo-white* being, for instance, such a combination, which can scarcely be removed from tissues prepared from animal fibres (sheep-wool and silk).

Writing executed with a metallic salt can, with comparative ease, be removed from a tissue without leaving a trace behind. Silver is dissolved by potassium-cyanide solution, and gold and platinum by chlorine-water; but writing executed with indigo-white, with an addition of carbon, is almost indestructible, because even after accomplishing the destruction of the indigo-white, the carbon adheres so firmly to the fiber that it eannot be removed by any agent.

METALLIC MARKING INKS.—A. Silver marking ink. —There are many directions for the preparation of marking ink, the basis of which consists of silver, and the most approved of them will be given in the following :—

The nitrate of silver is exclusively used for the preparation of these inks. This preparation, also known in commerce under the name of *lunar caustic*, being generally sold at a high price, it is advisable for the manufacturer who uses large quantities of it to prepare it himself, which is readily effected according to one of the directions given below.

Preparation of nitrate of silver.—The nitrate of silver to be used for marking ink should be absolutely free

# THE MANUFACTURE OF INK.

from copper. A perfectly pure preparation is obtained as follows:—

Bring the silver to be dissolved into a glass vessel and pour pure nitric acid over it. The silver is energetically attacked by the acid and rapidly dissolved, whereby redbrown fumes of a pungent odor are evolved. According to whether the silver used contained more or less copper, a solution of a more or less blue color is obtained (the silver salt is colorless, but the nitrate of copper blue).

To the solution of the silver in nitric acid, now add hydrochloric acid as long as a white, caseous precipitate of chloride of silver is formed. The supernatant fluid (in which hydrochloric acid should no longer produce turbidity) is poured off, and the precipitate washed upon a paper filter with pure rain-water until a small quantity of the filtered fluid gives not a trace of a blue coloration with ammonia, which indicates the absence of copper.

Now bring the washed precipitate of chloride of silver into a glass vessel, pour a small quantity of water and hydrochloric acid over it, and put pieces of zine in the vessel. The chloride of silver soon changes its color, which passes into a peculiar metallic gray, metallic silver being separated from the chloride of silver. After a few days, filter the mass, wash the *pure silver* remaining upon the filter with rain-water as long as the filtrate shows a white turbidity with ammonia, and then dissolve the *pure silver powder* in nitric acid, which must be free from any admixture of hydrochloric acid, otherwise flakes of chloride of silver would again be formed in the solution.

The solution is carefully heated in porcelain capsule; but heating, which is best done over an alcohol or gas

flame, must not be carried to the boiling point, otherwise loss by squirting might be incurred.

When the solution has been entirely evaporated, a white crystalline mass remains behind. The fire is then increased, and the crystalline mass fused, after which it is allowed to congeal.

By operating in the above-described manner, the nitrate of silver is obtained in the form of a colorless crystalline mass, which gradually blackens when exposed to light, and when dissolved in water leaves no residue. It must be kept in a dark place.

From the metal alloyed with copper, pure nitrate of silver may be prepared as follows : The alloy is dissolved in nitric acid, the solution evaporated to dryness, and the mixed nitrate cautiously heated to fusion. A small portion of the melted mass is from time to time removed for examination; it is dissolved in water, filtered, and ammonia added to it in excess. While any copper salt remains undccomposed, the liquid will be blue, but when that no longer happens, the nitrate may be allowed to cool, dissolved in water, and filtered from the black oxide of copper.

It is always necessary to fuse the nitrate of silver obtained by either method, since, to the mass obtained by evaporation only, sufficient nitric acid adheres to destroy the tissue marked with such a solution.

Preparation of the tissue for marking ink.—Tissues may be directly marked with a solution of nitrate of silver in rain-water, but the characters thus obtained run as if written upon blotting-paper, and besides do not very tenaciously adhere to the fibre of the tissue.

By previously coating the portion of the tissue— $\frac{12}{12}$ 

whether linen, cotton, silk, or wool—which is to be marked with a size, the finest writing or drawings can be executed without danger of running.

To prepare the tissue for the reception of writing use: Crystallized soda 1, gum-arabic 1, water 10.

Dissolve, with the assistance of heat, the gum-arabic and the soda in the water, filter the solution and keep it in bottles. For use pour a sufficient quantity of it in a vessel, dip the place of the tissue to be marked in it, and, after allowing the fluid to drain off, dry the tissue. When perfectly dry, smooth it by running a hot flatiron over it.

The solutions of nitrate of silver and other silver salts in water being colorless, they are colored for the purpose of using them as inks, and of recognizing what has been written with them, with an indifferent coloring matter, which exerts no influence upon the silver salt itself.

Silver marking ink.—Nitrate of silver 2, water 20, gum-arabie 2, lamp-black 1.

Dissolve the gum-arabie by itself in 10 parts of the water, and earefully rub the solution with the lampblack. Then dissolve the nitrate of silver in the remaining 10 parts of water, and intimately mix both solutions by shaking.

The only purpose of the addition of lamp-black being to render the writing immediately visible, any other substance may be substituted for it, very finely-pulverized indigo or a solution of sap-green being very suitable for the purpose.

After marking with the ink, place the tissue in a light place, best where it is exposed to the direct rays of the sun. The nitrate of silver is thereby decomposed, very

finely-divided silver, which produces the black color, being separated. The nitric acid, which is at the same time liberated, is neutralized by the soda contained in the preparation; if the latter were not present, the tissue, especially if very fine, might be eaten through.

After a few days, when the writing has become as dark as possible, wash the marked place with clean warm rain-water. The tissue may then be washed in strong lye without injury to the writing.

It may here be remarked that for writing with metallic inks steel-pens should not be used, the steel aeting upon the silver or gold solution so that metal is separated on the pen and iron dissolved instead. The writing thereby acquires not only a paler color, but frequently a rust-colored rim, which is caused by the dissolved ferric oxide. Horn- or quill-pens should be employed, and thoroughly washed with rain-water after use.

Ammoniacal silver inks.—By adding aqua ammoniæ to a solution of nitrate of silver in water, a precipitate of hydroxide of silver is formed, which, by the addition of more aqua ammoniæ, is redissolved, and then forms a solution of ammonio-nitrate of silver. The ammonionitrate of silver has the advantage of yielding an ink which remains clear and deposits no sediment, as is the case with ink containing simply nitrate of silver.

Normal ammoniacal silver ink.—Nitrate of silver 6, gum-arabic 6, soda 8, rain-water 15, aqua ammoniæ 12.

Dissolve the nitrate of silver in a flask in the water, add the ammonia to the solution, and finally the gum and the soda. Then place the flask in a pot filled with water, and heat until the fluid has acquired such a dark-

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brown color that writing executed with it is immediately visible.

During heating close the flask loosely, so that the excess of ammonia can escape. Heating, however, must not be carried too far, otherwise too much ammonia volatilizes, so that the total quantity of silver does not remain in solution, and a precipitate is formed. For the same reason the bottles containing the finished ink must be well closed and kept, like every other silver or metallic ink, in a dark room.

Ink, prepared according to the above directions, is especially suitable for writing and drawing with the pen; should it be too thinly-fluid, add some gum-arabic solution.

Silver stamping ink.—Nitrate of silver 10, aqua ammoniæ 20, soda 20, gum-arabic 25, water 80.

Dissolve the nitrate of silver in the aqua ammoniæ, and the soda and gum-arabic in the water. Mix the two solutions, and heat until the at first turbid fluid has acquired a beautiful brown color, and has become perfectly clear.

For writing with the pen, the ink may immediately be used after it becomes brown; but for stamping it is recommended to somewhat decrease the quantity of water, whereby a more concentrated fluid is obtained, which yields beautiful, sharp impressions.

For hotels, bath-houses, hospitals, and all places requiring large quantities of linen, there is no better marking ink than the above, since a sharp and durable impression, of even quite small characters, is obtained by one pressure of the stamp.

Absolutely indelible ink.—The following, according to the *Pharmaceutische Zeitung*, is the formula for the indelible marking ink used in the German marine and naval service :—

Nitrate of silver 125, liquor ammoniæ 250, soda (commercial) 175, mucilage of acacia 375, boiling water 125.

Dissolve the nitrate of silver in the ammonia in one vessel, and in another dissolve the soda in the boiling water, and mix the solutions. Finally, add the mucilage, and place the mixture in the sun until it turns brown.

*Cheap silver ink.*—The silver inks given above are quite expensive, since a strongly-concentrated solution of nitrate of silver has to be used to obtain deep-black writing. The same object may, however, be attained without the use of much silver, by employing copper salts in connection with nitrate of silver.

By compounding a copper salt with ammonia, a paleblue precipitate of cupric hydrate is at first formed, which, with an excess of ammonia, is, however, redissolved to ammonio-cupric oxide, possessing a beautiful azure color. By heating writing executed with such ink—for instance, by placing upon it a hot flat-iron the cupric oxide, which represents a deep-black powder, is separated.

Hence, by preparing inks containing mixtures of ammonio-nitrate of silver and ammonio-cupric oxide, the product will yield beautiful black and durable writing.

Nitrate of silver 15, cupric sulphate (blue vitriol) 35, ammonia 50, gum-arabic 20, soda 20, rain-water 80.

Dissolve the nitrate of silver and the cupric sulphate in 40 parts of water, and add to the solution the ammonia, whereby a beautiful dark-blue clear solution is formed. If the solution should not be entirely clear, add more ammonia.

Dissolve, with the assistance of heat, the gum-arabic and soda in the remaining 40 parts of water, and combine both solutions. On account of the dark-blue color of this ink, the addition of a special coloring matter is not required.

This ink is excellent for linen and white tissues of silk and wool; for thin cotton tissues, etc., the quantity of gum-arabie has to be somewhat inercased.

Silver drawing inks.—For the execution of entire drawings upon tissues with silver inks, it is best to use special eompositions; and a few formulas for preparing such inks, which may also be used for stamping, are here given :—

Nitrate of silver 20, soda 30, water 100, tartarie aeid 7, litmus 5, gum-arabie 40.

This ink is produced by first preparing anmoniotartrate of silver. For this purpose, first dissolve the nitrate of silver in 40 parts of water and the soda in 60 parts of water. Then add soda solution to the silver solution as long as a precipitate of carbonate of silver is formed. This white precipitate is filtered off, thoroughly washed with rain-water, and triturated with the tartarie aeid in a mortar, a small quantity of water being added. The mass thereby effervesces, on account of the carbonie aeid being expelled by the tartarie aeid.

To dissolve the tartrate of silver formed, earefully add ammonia, then the aqueous extract of litmus, which gives to the ink a blue color, and, after stirring thor-

oughly, the gum-arabic solution; then dilute as much as necessary.

Red silver drawing ink.—Nitrate of silver 12, tartaric acid 15, gum-arabic 10, carmine  $\frac{1}{2}$ , water 20.

Triturate the nitrate of silver, which should be entirely dry, with the tartaric acid, and pour the ammonia over the powder, stirring frequently. No more ammonia than required for solution should be used. The clear solution is mixed with the gum-arabic solution, and suitably diluted with water.

Kindt's green silver ink.—Nitrate of silver 11, ammonia 22, soda 22, water 12, gum-arabic 50, sap-green 2.

According to Kindt's directions, the ink is prepared by dissolving the nitrate of silver in the ammonia, combining the solution with the soda solution, prepared by boiling, and finally adding the gum and sap-green.

However, according to experiments made, the following method is to be preferred :---

Dissolve the nitrate of silver in the ammonia, shake the solution with the soda, and add the gum-arabic solution and the sap-green.

This ink becomes black only very gradually if exposed to the light. The change into black may, however, be accelerated by passing a hot flat-iron over the dry writing.

Chloride of silver ink.—A. Nitrate of silver 1, water 10, gum-arabic 2, indigo-carmine  $\frac{1}{4}$ .

B. Common salt 2, gum-arabic 5, water 10.

Prepare the two fluids, A and B, the latter (B) serving for the preparation of the tissue, and the former (A) for writing. When the latter is dry, expose it to the sun, whereby in a short time it acquires an intensely-black color, the chloride of silver formed rapidly turning black when exposed to the light.

B. GOLD INKS.—Gold when brought in contact with organic substances very readily separates in a metallic state from all its combinations, and can be advantageously used for writing upon tissues. The high price of gold is, however, an obstacle to the general use of thesc otherwise excellent inks, which yield writing very difficult to remove.

Black gold ink.—Reade has recommended a process for the preparation of this ink, but one of the most necessary ingredients—the iodide of ammonium—has to be prepared in such a manner that a considerable quantity of nitrogen iodide, which, when dry, explodes with the slighest touch, is readily formed.

The iodide of ammonium required for the preparation of this ink may, however, be prepared in a manner which entirely excludes the formation of nitrogen iodide, and is therefore devoid of danger.

Ammonia is first introduced into sulphuretted hydrogen, which is obtained by pouring sulphuric acid over ferrous sulphide, ammonium sulphide being thereby formed. The iodine is then dissolved in the ammonium sulphide. The fluid assumes a milky turbidity by the iodine separating sulphur from the ammonium sulphide and combining with the ammonium.

The colorless solution of iodide of ammonium is filtered off from the separated sulphur, and after dissolving more iodine in it, immerse in the fluid genuine gold leaf, which rapidly dissolves in it. The resulting solution consists of a double salt of iodide of gold and iodide of ammonium.

By writing with this fluid alone upon a tissue, brownishblack characters are obtained, but a mixture of the gold solution, with one of the ammonical silver inks, previously mentioned, yields black writing.

Gold purple ink.—A. Aurochloride of sodium 1, water 10, gum-arabic 1.

B. Tin-salt 1, water 100, gum-arabic 10.

Solution A constitutes the actual ink, and serves for writing, while solution B serves for preparing the tissue.

The solution of aurochloride of sodium is prepared as follows: Dissolve gold in hydrochloric acid, to which, from time to time, add some nitric acid; for 4 parts of hydrochloric acid 1 part of nitric acid is required. The impure (cupriferous) solution is evaporated to a small bulk, to remove the excess of acid, then diluted with water, and, with the assistance of heat, mixed with a solution of oxalic acid, whereby the gold is separated in the form of a delicate-brown powder.

After washing, the pure gold is dissolved in a mixture of hydrochloric and nitric acids, and the solution mixed with common salt. After evaporation, the fluid yields crystals of aurochloride of sodium.

Previous to writing, prepare the tissue with the tinsalt (hydrated chloride of tin) solution, and then write with the gold solution. The so-called purple of Cassius is thereby formed in the tissue, and its color is, as a rule, the more delicate the more dilute the solutions are.

Gold lustre ink.—To obtain with gold solution, writing which shows the natural lustre of gold, it is necessary to mix with the mass, used for the preparation of the tissue, a body possessing the property of immediately separating the gold in a metallic state from the gold solution. Oxalic acid possesses this property. Prepare the following solutions :---

A. Aurochloride of sodium 1, gum-arabic 2, water 10.

B. Oxalic acid 2, gum-arabic 4, water 10.

B is used for preparing the tissue, and A for writing. After the writing appears, smooth the tissue by strong pressure and wash it.

C. PLATINUM INKS.—If metallic platinum is dissolved in a mixture of hydrochloric and nitric acids, and the solution evaporated, a mass consisting of platinum chloride is obtained. Writing executed with a solution of platinum chloride upon a fabric will show a blackishgray color, but with the simultaneous use of tin-salt red characters are obtained.

Black platinum ink.—A. Platinum chloride 1, gumarabic 2, water 10.

B. Oxalic acid 3, gum-arabic 3, water 10.

A serves for writing, B for preparing the tissue. When the writing is dry and perfectly plain, wash the fabric.

Osmium marking ink.—On writing upon a fabric with a dilute solution of osmic acid in water—1 part in 50—the marks will soon assume an intense dark-blue color, and will be found to be very permanent. The osmic acid solution must be quite dilute, because stronger solutions are apt to destroy the fabric itself, and the latter must be previously mordanted and ironed. Quillpens or gold-pens should be used for writing.

D. VEGETABLE MARKING INKS.—Besides solutions of metallic salts, there are several organic bodies capable of producing writing of different colors upon tissues. The use of these substances is actually to be preferred to

that of the metallie preparations, because they are not only eheaper, but, under certain conditions, also more durable, since writing executed with the salts of gold, platinum or silver can be gradually rendered invisible by careful treatment with potassium cyanide solution or dilute acids.

Writing of various eolors could be readily produced upon fabries; it would only be necessary to mordant the fabrie with hydrated chloride of tin (tin-salt) or a pure salt of alumina, and to prepare it with the decoetion of a coloring matter—eochineal, logwood, madder, etc. From the coloring matter and the tin-salt or alumina, salts—so-called lakes—of the corresponding colors would be formed.

For fabrics which are not to become wet, the formation of such combinations for the production of writing might be utilized—in fact, the printing of tissues is based upon it. However, for fabries which are to be frequently washed, such writing fluids are not suitable, since, by the chemicals, especially the soap and lye, used in washing, the writing would soon be destroyed.

There are, however, some organic coloring matters which are capable of resisting the action of lye, and are, therefore, very suitable for the preparation of marking inks, *indigotin*, the coloring matter of the cashew-nut, and aniline black being especially adapted for the purpose.

Indigotin marking ink.—The blue eoloring matter indigotin—oeeurring in indigo, possesses the property of being eonverted by the action of eertain substances into. a colorless combination ealled *hydro-indigotin* or *indigowhite*, which, however, ean only exist when excluded from the access of oxygen. When exposed to the air, it

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is rapidly reconverted into indigo-blue or indigotin, which is only soluble in furning sulphuric acid.

To prepare *indigo-white* proceed as follows: Put 5 parts of finely-powdered indigo in a flask, add 10 parts of ferrous sulphate (green vitriol), and pour over it a solution of 10 parts of caustic soda in 50 of water. Cork the flask and set it aside for a few days, shaking frequently. If, after shaking, the fluid shows no longer a blue coloration, the conversion of the indigo-blue into indigo-white is finished.

Now, have in readiness a bottle containing 5 parts of gum-arabic and  $\frac{1}{4}$  part of finely-pulverized litmus, quickly add the solution of indigo-white, and close the bottle tightly. To dissolve the gum, shake the bottle. The solution thus obtained forms the writing ink.

For use, dip the pen into the fluid, and after writing upon the fabric, which does not require special preparation, immediately close the bottle. On exposure to the air the writing gradually becomes greenish, and then pure indigo-blue. It can be destroyed only by chlorine or nitric acid. After standing for sometime a dark-blue powder, which is pure indigotin, is separated from the solution of indigo-white in the bottle. This indigotin may be again used for the preparation of indigo-white.

Cashew-nut ink.—The cashew-nut is the fruit of Anacardium occidentale, a small tree which is indigenous to tropical America, and has been naturalized in some portions of Africa and the East Indies. The fruit is about an inch long, somewhat less broad, and about  $\frac{1}{3}$  inch thick. It is kidney-shaped, convex on the back, with a sear on one of the rounded ends, of a gray-brown color, and inodorous.

The substance which gives to the eashew-nut its coloring principle is partially of the nature of a volatile oil and partially that of a resin. It is obtained by treating the eoarsely-bruised nuts with alcohol and ether, or, still better, with petroleum-ether, the process being as follows:—

Pour petroleum-ether over the eoarsely-bruised nuts in a bottle, and close the latter with a well-fitting cork. Shake frequently, and after a few days filter the solution, which has been formed, into a dish, and set it aside, well protected from dust, until converted into a syrupy mass. This extract being of a consistency suitable for writing or for use as a stamping ink, it is, as a rule, only necessary to mix it with mucilage.

Writing executed with it upon linen or cotton fabrics, is at first dirty-brownish, but on being brought in contact with alkalies, in a short time assumes a deep-black color.

To produce with this preparation durable writing, hold the fabric, immediately after the execution of the writing, over a vessel containing liquid ammonia. By the action of the latter the writing appears with an intense black color, and is so durable that the fabric may be washed in chloride of lime solution, or even be dipped in dilute nitric acid, without in the least changing the writing.

Black copper marking ink for linen.—Add to a solution of chloridc of copper potash lye as long as a precipitate is formed; then pour off the fluid, dissolve the precipitate in the smallest quantity of ammonia possible, and add sufficient dextrin that the fluid can be used for writing with a quill-pen without running. Run a hot flat-iron over the dry writing, whereby it acquires a black color.

Aniline marking inks.—Aniline black may be used for the preparation of an excellent marking ink, which answers all demands. Other aniline colors, such as red, green, blne, and violet, are not suitable for the purpose, because, though very beautiful, they are not very permanent, and rapidly disappear, especially when subjected to the action of alkalies, as in washing.

For the preparation of aniline marking inks various formulas have been proposed, the best of which are here given.

Copper aniline marking ink.—A. Chloride of copper 15, sal-ammoniac 10, chlorate of sodium 20, water 100.

B. Hydrochlorate of aniline 25, gum-arabic 20, glycerin 5, water 50.

Prepare each solution (A and B) by itself, and mix 5 parts of solution B with 1 part of solution A, whereby a greenish fluid is formed, which, however, soon becomes black on exposure to the air, and is then no longer fit for writing. The fluids should, therefore, be mixed only immediately before writing. To give the writing durability, it is fixed upon the fabric by holding it, when dry, over boiling water, until the portion of the fabric upon which it has been executed is thoroughly moistened. Writing thus treated remains unchanged, no matter how often the fabric may be washed, and even resists for a long time the action of chloride of lime.

Marking ink for linen according to Jacobsen.—I. Crystallized chloride of copper  $4\frac{1}{4}$  drachms, chlorate of sodium  $5\frac{1}{4}$  drachms, sal-ammoniac  $2\frac{1}{4}$  drachms, distilled water 2 ozs.

II. Glycerin 5 drachms, mixed with 10 drachms of a solution of 1 part of gum-arabic in 2 of water, hydrochlorate of aniline 11 drachms, dissolved in 1 oz. of distilled water.

Immediately before use, mix 1 part of solution I with 4 parts of solution II. Writing executed with the greenish fluid thus obtained becomes black in a few days, and cannot be removed by ehemical agents.

Aniline stamping ink.—A. Chloride of copper 1, ammonia 40, common salt 1.

*B.* Hydrochlorate of aniline 40, gum-arabic 15, gly-cerin 15, water 30.

For use, mix 4 parts of solution A with 1 of solution B. The writing is fixed by placing a hot flat-iron upon it for a few minutes.

Black aniline marking ink.—Aniline black 27 grains, 95 per cent. alcohol 1 oz. 7 drachms, hydrochloric acid 60 drops, gum-arabic 38 grains, water 6 ozs.

Triturate the aniline black, first with the alcohol and hydrochloric acid, and then with the gum-arabic solution. The mixture yields a very intense black ink, which, however, blots on moistening. In order to use it for marking linen, substitute for the gum-arabic solution, one consisting of shellae 38 grains and alcohol 6 ozs.

This ink is not attacked by water, and may be used for marking fabrics and for writing upon wood, glass, metal, leather, and caoutchouc.

Since the introduction of the vegctable marking inks, the use of metallic inks has much decreased, they being more expensive. However, they deserve the preference, since they are absolutely indifferent towards the action

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of alkalics used in washing; but, on the other hand, they can be completely removed from the fabric by means of a solution of potassium cyanide in water. Writing executed with silver inks can also be removed by very dilute nitric acid, but gold and platinum only by fluids containing free chlorine.

Writing absolutely indestructible is obtained by marking the fabric by means of a glass rod, drawn out to a fine point, dipped in concentrated sulphuric acid, and washing the fabric as soon as the writing is brown. A portion of the fabric is thereby carbonized, and thus an indestructible writing produced. However, the execution of such writing requires considerable experience, since, if the sulphuric acid is allowed to act too long, holes may readily be eaten in the fabric.

# XXV.

#### INK SPECIALTIES.

IN some industries the use of fluids for writing upon metal, leather, wood, ivory, etc., is required.

Inks for writing upon metal—Black ink for writing on metal.—Copal 10, oil of turpentine 12, lamp-black 2.

Melt the copal in an iron ladle over a coal fire. When melted, increase the heat until the copal begins to decompose, with the expulsion of thick, heavy vapors. In case the mass should ignite, immediately extinguish the flame by placing upon the ladle a well-fitting lid kept on hand for that purpose.

When the copal has been reduced to about  $\frac{4}{5}$  of its

original bulk, take the ladle from the fire, and, after allowing the mass to cool somewhat, add a small quantity of the oil of turpentine. In doing this great care has to be exercised, since, if the temperature of the mass is too high, the oil of turpentine will be ejected. Then add the remaining oil of turpentine, with constant stirring, and finally stir in the lamp-black. If, after cooling, the mass should be too thickly-fluid, add oil of turpentine until it has the proper consistency for writing. The finished ink, drying rapidly on exposure to the air, must be kept in well-closed vessels.

This ink can be used for writing on any kind of metal, the writing adhering especially well if the metallic surface is very bright and at the same time somewhat rough, which is effected by rubbing the place where the writing is to be executed with shave-grass.

Red ink for writing on metal.—Copal 20, oil of turpentine 24, cinnabar 2.

This ink is prepared in precisely the same manner as the preceding, but the addition of oil of turpentine should not be carried too far, otherwise the cinnabar, which is specifically very heavy, might readily deposit.

Colored ink for writing on metal.—With the use of the above-described basis-mass, ink of almost any color may be produced, Brunswick green being used for green, ultramarine for blue, chrome yellow for yellow, and aniline violet for violet.

Dull-black inks for writing on metal.—Cupric sulphate (blue vitriol) 10, vinegar 2, gum-arabic 4, lamp-black 2, water 10.

With this ink, beautiful dull-black writing can be executed on bright iron, zinc, and brass, but not on

copper and tin. For the latter two serves the following mixture :---

Cupric sulphate 10, hydrochloric acid 4, gum-arabic 4, sal-ammoniac 8, lamp-black 2, water 10.

Ink for writing on silver.—Dissolve 1 part of aurochloride of sodiam in 15 of water, and write or draw with the solution on the *bright* silver, beautiful goldbrown characters being immediately formed. If the writing is to retain this color, dip the article in liquid ammonia, and then rinse off in water. If, however, the writing is to be black, place the article in the sun, whereby the gold-brown color is rapidly converted into black.

*Black* writing on silver may also be produced with a solution of platinum chloride, prepared by dissolving metallic platinum in a mixture of nitric and hydro-chloric acids.

By tracing engravings on silver with one of these inks, the article acquires an appearance resembling niello work.

Ink for black writing on zinc.—Cupric sulphate 1, chlorate of potassium 1, water 36.

By writing with the solution, using a quill-pen, upon the *bright* zinc, black characters are immediately obtained. When dry, wash the zinc with pure water, and pass an oily rag over the writing.

Black ink for writing on leather.—A. Nut-galls 10, gum-arabic 1, water 100.

B. Ferrous sulphate (green vitriol) 1, gum-arabic 2, indigo-carmine  $\frac{1}{2}$ , water 10.

Apply solution A to the portion of the leather to be written on, and when dry write with solution B. The

writing produced in this manner has a beautiful black color and penetrates deeply into the leather, especially if the lower side of it has been thoroughly moistened.

Black ink for writing on fabrics of linen, cotton, wool, and silk.—Saturate the place to be written on with alum solution, and, after drying repeatedly, apply a decoction of nut-galls. Upon the fabric thus prepared, the finest writing may be executed with solution B, given in the preceding formula (black ink for leather). By somewhat increasing the quantity of indigo-carmine, the writing becomes much more durable.

Blue ink for writing on glass.—Bleached shellac 10, Venice turpentine 5, oil of turpentine 15, pulverized indigo 5.

Dissolve the shellac and Venice turpentine in the oil of turpentine by placing the bottle containing them in warm water; stir the finely-pulverized indigo into the solution.

This ink is not attacked by water.

Ink for use in laboratories.—Dissolve by boiling in 400 parts by weight of water 30 of borax, add to the solution 20 of shellac, boil again until the shellac is dissolved, and add to the clear fluid 10 parts by weight of nigrosine and 15 to 30 of ammonia.

This ink for a long time resists the destructive action of vapors frequently occurring in laboratories.

Ink for writing on ivory.—Not only indelible black writing and drawings may be executed upon ivory, but it is also possible to produce by a simple process all shades, from the darkest black, through brown, to the most delicate pale brown.

Previous to writing on it, the ivory has to be prepared, otherwise the ink would not adhere to the greasy surface. This preparation may be effected by laying the ivory in a strong soap solution, allowing it to remain for sometime. Liquid ammonia is still better for the purpose.

First prepare a normal ink composed of nitrate of silver 10, distilled water 100.

Divide this normal ink into ten equal portions. The portion designated No. 1 is left unchanged; No. 2 is mixed with an equal quantity of water, and consequently contains one-half the quantity of nitrate of silver in No. 1; No. 3 eontains for 1 part nitrate of silver solution 3 parts water, and so on.

The weaker the separate silver solutions, the paler the characters made with them will be. While No. 1 yields entirely black writing, that executed with No. 2 is paler with a grayish tinge, and that with No. 10 shows only a slightly gray color.

With the assistance of these silver inks of different strength, very tasteful designs may be executed upon the ivory by means of the pen as well as of the brush. The designs are indelible, and show gray to black shades of eolor.

If the drawing is to show a warm brown gold shade, place the ivory in a solution of aurochloride of sodium 1, water 100, and allow it to remain until the black eolor is changed to a gold brown. Then take the article from the gold solution and immediately place it in a solution of 1 part sodium hyposulphite in 10 parts water.

Ink for writing and drawing on wood.—By the skillful treatment of wood, especially that of a light eolor, beautiful effects may be produced with the assistance of various

inks, so that the designs thus executed appear at a distance like inlaid work.

In all cases, the wood has to be prepared, which is done by repeatedly coating it with a boiling solution of gelatine, and treating it with a solution which partially prevents the inks from penetrating too deeply, and partially serves as a basis for them. For this purpose use a solution prepared from—

Alum 10, tin-salt 10, hydrochlorie acid 2, water 50.

Repeatedly apply this solution by means of a sponge to the wood.

Upon the wood thus prepared all possible colors may be produced by the use of the following fluids :—

*Black*, by means of the cashew-nut ink, given on p. 188. When dry, pass a brush dipped in ammonia over the drawing.

Brown, with a solution of potassium permanganate in water.

Blue, with a deeoction of logwood.

*Red*, with an aqueous decoction of Brazil wood or with ammoniacal cochineal ink.

Yellow, with a decoction of French berries or with a solution of picric acid.

Show-card ink.—Pure asphaltum 16 ozs., Veniee turpentine 18 ozs., lamp-blaek 4 ozs., spirit of turpentine 2 quarts.

Dissolve and mix thoroughly.

Marking ink for packages.—Thoroughly mix lampblack with sufficient turpentine to make it thin enough to flow from the brush. Powdered ultramarine instead of lamp-black makes a fine blue marking ink for the same purpose. Marking ink for bales.—Shellae 2 parts by weight, borax 2, water 25, gum-arabic 2, Venetian red sufficient to color.

Boil the shellac and the borax in the water until solution is complete, add the gum-arabic, and take the vessel from the fire. When the solution has become cold, add sufficient Venetian red to bring it to a suitable consistency and color. This ink must be preserved in a glass or earthenware vessel.

Luminous ink.—Phosphorus  $\frac{3}{4}$  drachm, oil of cinnamon  $\frac{3}{4}$  oz. Mix, cork well, and heat gently until thoroughly combined. A letter written with this ink can only be read in a dark room; the writing will have the appearance of firc.

Ink for writing on photographs.—Iodide of potassium 10 parts, water 30, iodine 1, gum-arabic 1.

This ink will produce white lines on the dark background.

Cancelling ink for post-offices, etc.—A fine grade of printing ink is ordinarily employed. A good ink may be made as follows:—

Balsam of copaiba (pure) 9 ozs., lamp-black 3 ozs., indigo 5 drachms, Prussian blue 5 drachms, Indian red  $\frac{3}{4}$  oz., dried yellow soap 3 ozs.

Grind to a uniform smoothness.

Ink erasers.—I. Immerse blotting-paper or a similar material in a hot concentrated solution of citric acid, roll it into a pencil, and coat the larger portion of it with paper or lacquer. Moisten the eraser with water, and rub over the ink to be removed. Drop upon the ink spot a drop of water containing chloride of lime. The ink immediately disappears.

II. Mix equal parts of oxalic and tartaric acids in powder. When to be used, dissolve a little in water. It is poisonous.

III. Use equal parts of eream of tartar and eitric acid in solution with water.

IV. A more powerful one than the preceding is a saturated solution of oxalic acid in water. The red inks are made of various bases for the color, as Brazil wood, cochineal and aniline red. The aniline red may be removed by alcohol acidulated with nitric acid. There is no receipt for the other reds.

V. Chloride of lime  $\frac{1}{2}$  lb. is added to 2 quarts water. Allow this to stand for 24 hours; then strain, and add 1 drachm of acetic acid to every ounce of the ehloride of lime used. Apply this liquid to the blot without rubbing. When the ink has disappeared, absorb the fluid with blotting-paper.

Inks for zinc labels.—I. Take 1 drachm verdigris, 1 drachm powdered sal-ammoniac, and  $\frac{1}{2}$  drachm lampblack, and mix them with 10 drachms water. This will form an indelible ink for writing on zinc.

II. E. Dieterich gives the following as a reliable formula: Chloride of potassium 3 parts, sulphate of copper 6, distilled water 7. Dissolve and mix with the following :—

Water-soluble aniline blue  $\frac{1}{20}$  part, dilute acctic aeid 5, distilled water 20.

Permanent ink for writing in relief on zine.—Dry bichloride of platinum 1 part, gum-arabic 1, distilled water 10. The letters traced upon the zine with this solution turn black immediately. The black characters resist the action of weak acids or of rain, and the liquid is thus adapted for marking signs, labels, or tags, which are liable to exposure. To bring out the letters in relief, immerse the zinc tag in a weak acid for a few minutes. The writing is not attacked, while the metal is dissolved away.

*Type-writer ribbons.*—Mr. Isidor Furst, in the "Ameriean Druggist," gives the following directions :—

The constituents of an ink for type-writer ribbons may be broadly divided into four elements: 1, the pigment; 2, the vehicle; 3, the corrigent; 4, the solvent. The elements will differ with the kind of ink desired, whether permanent or copying.

Permanent (record) ink .- Any finely-divided nonfading color may be used as the pigment; vaseline is the best vehicle, and wax the eorrigent. In order to make the ribbon last a long time with one inking, as much pigment as possible should be used. Suppose we wish to make black record ink. Take some vaseline, melt it on a slow fire or water-bath, and incorporate, by constant stirring, as much lamp-black as it will take up without becoming granular. Take from the fire and allow it to eool. The ink is now practically finished, except, if not entirely suitable on trial, it may be improved by adding the corrigent, wax, in small quantity. The ribbon should be eharged with a very thin, evenlydivided amount of ink. Hence, the necessity of a solvent, in this instance a mixture of equal parts of petroleum benzin and reetified spirits of turpentine. In this mixture dissolve a sufficient amount of the solid ink by vigorous agitation to make a thin paint. Try your ink on one extremity of the ribbon; if too soft, add a little wax to make it harder; if too pale, add more coloring

matter; if too hard, add more vaseline. One seeret of success lies in the proper application of the ink to the ribbon. Wind the ribbon on a piece of cardboard, spread on a table several layers of newspaper, then unwind the ribbon in such lengths as may be most convenient, and lay it flat on the paper. Apply the ink after agitation, by means of a soft brush, and rub it well into the interstices of the ribbon with a tooth-brush. Hardly any ink should remain visible on the surface.

On the same principle, other colors may be made into ink, but for delicate colors albolene and bleached wax should be the vehicle and corrigent, respectively.

The various printing inks may be used if properly corrected. They require the addition of vaseline to make them non-drying on the ribbon, and of some wax if found too soft. Where printing inks are available, they will be found to give excellent results if thus modified, as the pigment is well milled and finely divided.

After having thus explained the principles underlying the manufacture of permanent inks, we can pass more rapidly over the subject of copying inks, which is governed by the same general rules.

For copying inks, aniline colors form the pigment; a mixture of about 3 parts of water and 1 part of glycerin, the vehicle; transparent soap (about  $\frac{1}{4}$  part), the corrigent; stronger alcohol (U. S. P.) about 6 parts, the solvent. The desired aniline color will easily dissolve in the hot vehicle, soap will give the ink the necessary body and counteract the hygroscopic tendency of the glycerin, and in the stronger alcohol the ink will readily dissolve, so that it can be applied in a finely-divided state to the ribbon, where the evaporation of the alcohol

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will leave it in a thin film. There is little more to add. After the ink is made and tried—if too soft, add a little more soap; if too hard, a little more glycerin; if too pale, a little more pigment. Probably, printer's *copying* ink can be utilized here likewise, because every one now has the means to modify and correct it to make it answer the purpose.

Users of the type-writer should so set a fresh ribbon as to start at the edge nearest the operator, allowing it to run back and forth with the same adjustment, until exhausted along that strip; then shift the ribbon forward with the width of one letter, running until exhausted, and so on. Finally, when the whole ribbon is exhausted, the color will have been equally used up, and on reinking, the work will appear even in color, while it will look patchy if some of the old ink has been left here and there, and fresh ink applied over it.

# XXVI.

### SYMPATHETIC INKS.

WHILE the writing fluids known under this name are of little practical value, except perhaps that they favor secret correspondence, they are very interesting from a chemical point of view.

The term sympathetic inks is applied to fluids which, when subjected to a certain treatment, either change their color, appear or vanish. Some of the sympathetic inks consist of one fluid only; others of two, viz., the writing fluid and the developer.

Yellow sympathetic inks.—I. Dissolve copper in hydrochloric acid to which a small quantity of nitric acid has been added. Dilute the solution so that on writing with it, invisible characters are obtained. On heating the paper the characters acquire a beautiful yellow color, but disappear on cooling.

II. Dissolve antimony in a mixture of hydrochloric and nitric acids, and write with the solution. By applying a decoction of nut-galls to the writing it becomes visible, showing a beautiful yellow color.

Sympathetic gold ink.—Write with a not too dilute solution of aurochloride of sodium and treat the paper with a solution of 1 part oxalic acid in 10 of water, whereby the characters appear in an unchangeable gold color, and especially, by smoothing the paper, acquire a beautiful metallic lustre.

Red sympathetic ink.—This requires two fluids, one for writing and the other for developing the heretofore invisible characters. Write on the paper with a very dilute solution of aurochloride of sodium. When the writing is dry, pass a sponge dipped in a solution of tin-salt (hydrated chloride of tin) over it.

By the tin solution coming in contact with the gold solution, a combination of a purple color known as purple of Cassius is formed. The color is the more beautiful, the more dilute the solutions used.

The writing may also be made to immediately appear with a purple color by first immersing the paper in the tin-salt solution, allowing it to drain off, and drying. In the same manner writing executed with sympathetic ink consisting of two fluids may be made to immediately appear in its respective color.

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Vanishing purple ink.—Write with a very dilute solution of iron in a mixture of hydrochloric and nitric acids, and lay the paper, upon which no characters are visible, in a vessel in which stands a watch crystal containing a few drops of sulphocyanide of potassium, to which a small quantity of sulphuric acid has been added. The writing soon appears with a beautiful purple color. By holding the paper over water of ammonia, the writing again completely vanishes.

Green sympathetic inks.—According to their composition a distinction is made between green sympathetic inks consisting of one or of two fluids.

Simple green sympathetic ink.—Add to a solution of cobaltous nitrate (which is beautiful red at the ordinary temperature, but turns blue on heating) a certain quantity of nickel nitrate. The writing after drying is scarcely visible, but on gently heating the paper, for instance, on a stove or over a lamp, it appears with a very beautiful green color, which, however, disappears in a short time after cooling. The shade of green may be varied by the addition of a larger or smaller quantity of the nickel salt to the cobaltous nitrate solution.

Green sympathetic ink with two fluids.—Write with a solution of sodium chlorate in water. On passing a sponge dipped in cupric sulphate solution over the dry writing, it immediately appears with a bright green color, which is permanent.

Blue sympathetic ink.—Many cobalt salts have the property of forming crystals which, at the ordinary temperature, possess a beautiful red—generally rose-red or dark red—color, which on heating becomes blue. Hence every soluble cobalt salt may be used as a sympa-

thetic ink, the chloride and nitrate being mostly employed for the purpose. Characters written with solutions of these salts are almost invisible at the ordinary temperature, but on heating they appear dark blue, vanishing, however, again on cooling.

It is said that Theophrastus Paracelsus, a celebrated alchemist of the middle ages, was acquainted with the neat trick of changing by means of sympathetic ink a winter scene into a summer landscape. The branches of the trees are executed with ordinary brown paint, while the leaves are painted with vanishing cobalt-nickel ink. On heating the drawing the bare branches become clothed in green.

*Cobalt cyanide ink.*—Cobalt cyanide is especially distinguished by great sensitiveness to changes of temperature; paper saturated with the salt, when air-dry, shows a pale-red color, but turns blue with the slightest increase in temperature.

Cobalt cyanide is prepared by compounding a solution of sulphate of cobalt with a solution of sulphocyanide of potassium in alcohol as long as potassium sulphate is separated. The remaining solution of cobalt cyanide is then evaporated at a *very low* temperature. The pale-red writing executed with the solution immediately becomes blue on placing the paper upon the warm hand.

Brown sympathetic ink.—Potassium bromide 1, cupric sulphate (blue vitriol) 1, water 20.

On heating, the scarcely-visible writing appears with a beautiful brown color.

Black sympathetic ink.—Heat a cold saturated solution of oxalic acid to boiling, and add molybdic acid until no more is dissolved. Keep the fluid in black bottles. Writing executed with this colorless fluid becomes dark blue when exposed to the sun, and black on heating.

Invisible ink according to C. Widemann.—Intimately mix linseed oil 1 part, water of ammonia 20 parts, water 100 parts.

The mixture must be agitated each time before the pen is dipped into it, as a little of the oil may separate and float on top, which would, of course, leave an oily stain upon the paper. To make the writing or drawing appear, which has been made upon paper with the ink, it is sufficient to dip it into water. On drying, the traces disappear again, and reappear by each succeeding immersion.

Encre pour les dames (ink for ladies).—Under this name a proprietary article is sold in Paris. According to Hager, it consists of an aqueous solution of iodide of starch, and is especially intended for love-letters. In four weeks characters written with it disappear, preventing all abuse of letters, and doing away with all documentary evidence of any kind in the hands of the recipient.

Vanishing ink.—To make an ink black at the time of writing, but which will disappear after a short time, boil nut-galls in alcohol, put Roman vitriol and sal-ammoniac to it, and when cold dissolve a little gum in it. Writing done with this ink will vanish in 24 hours.

Various sympathetic inks.—I. Dissolve 15 parts of hydrochlorate of ammonia in 100 of water. Writing executed with this solution will appear when the paper is heated by holding it over a stove or by passing a hot flat-iron over it.

II. Writing executed with the juice of a lemon, onion,

leak, cabbage, or artichokc becomes very visible when the paper is heated.

III. Prepare a solution of acetate of lead in distilled water. Characters written with it will appear in black upon passing a solution of an alkaline sulphuret over the paper.

IV. Upon writing on paper that contains but little sizing with a very weak solution of starch, and submitting the dry characters to the vapor of iodine or passing over them a weak solution of iodide of potassium, the writing becomes blue, and disappears under the action of a solution of 1 part of hyposulphite of soda in 1000 of water.

V. Dilute an acid solution of chloride of iron until the writing is invisible when dry. This writing has the remarkable property of becoming red by sulphocyanide vapors (arising from the action of sulphuric acid on sulphocyanide of potassium in a long-necked flask), and it disappears by ammonia, and may alternately be made to appear and disappear by these two vapors.

# · XXVII.

### STAMP AND STENCIL INKS.

For stamping, inks of different colors are used, and their manufacture has, in modern times, become a branch of considerable importance. A good stamping ink should give a perfect impression of the characters engraved upon the stamp and remain fluid for sometime, *i. e.*, not dry upon the stamp, which would smear the

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engraving and cause the impression to be indistinct. The use of an ink which does not readily dry up is of special importance for rubber stamps, since they cannot be cleansed with the assistance of a brush, which would injure the sharp contours of the letters.

The use of ordinary printing ink has frequently been recommended for stamping, and it is quite suitable for the purpose, it yielding black and sharp impressions, which in a short time become dry. However, it has the disadvantage of drying too rapidly on the stamp itself, and, hence, can advantageously be used only when the stamp is in constant use, and requires to be frequently supplied with fresh ink.

This defect can, however, be remedied by mixing the printing ink with linseed oil. Printing ink 6 to 8 parts triturated with filtered linseed oil 1 part, gives an excellent stamping ink.

The addition of linseed oil should not be carried too far, otherwise the mass not only becomes too thinlyfluid and too pale, but also acquires the disagreeable property that the characters are surrounded by a transparent oily edge.

Black stamping ink.—An excellent stamping ink which does not run and gives good impressions is obtained according to the following formula :—

Best lamp-black 10, gum-arabie 4, glycerin 4, water 3.

First, dissolve the gum-arabic in the water, mix the solution with the glycerin, and triturate the whole with the lamp-black. Glycerin possesses the property of absorbing moisture from the air, whereby the ink is kept fluid. For stamps with fine engraved lines, the

quantity of lamp-black is increased so as to obtain a somewhat more thickly-fluid mass.

Colored stamping ink.—By substituting for the lampblack suitable substances of different colors, colored inks are obtained; for instance, *yellow*, with chrome-yellow; *red*, with minium or ocher; *green*, with Brunswick green; *blue*, with indigo, ultramarine, or Prussian blue; *brownred*, with colcothar; *brown*, with umber, etc.

White stamping ink.—A white "ink" for stamping embroidery patterns may be made by the following formula :—

Rosin 2 drachms, benzine 4 ozs., zinc-white  $\frac{1}{2}$  oz., or a sufficient quantity.

Dissolve the rosin in the benzine, triturate the zincwhite in a portion of the liquid to a smooth paste, and mix all together.

The proportions of the ingredients may be somewhat varied according to the views of the party using the mixture. The "ink" must, of course, be frequently shaken during use, to keep the pigment in suspension.

Stamping ink according to Dr. W. Reissig.—Dr. Reissig, of Munich, has recently made an ink for cancelling stamps which is totally indelible, and the least trace of it can be detected chemically. It consists of 16 parts of boiled linseed oil varnish, 6 parts of the finest lampblack, and 2 to 5 parts of iron perchloride. Diluted with  $\frac{1}{8}$  the quantity of boiled oil varnish, it can be used for a stamp. Of course it can only be used with rubber stamps, for metallic type would be destroyed by the chlorine in the ink. To avoid this, the perchloride of iron may be dissolved in absolute alcohol, and enough pulverized metallic iron added to reduce it to the proto-

chloride, which is rapidly dried and added to the ink. Instead of the chloride, other salts of protoxide or peroxide of iron can be used. The iron unites with the cellulose and the sizing of the paper, so that it can be readily detected, even after the ink has all been washed off. Sulphide of ammonia is well adapted for its detection.

Aniline stamping inks.—Beautiful stamping inks may be made from the various aniline colors, but their manufacture requires some skill. If the aniline color is to be used in a solid form, the preparation of the ink is very simple. Prepare a mixture of gum-arabic solution and glycerin in the proportions given under black stamping ink, p. 208, add a corresponding quantity of solid aniline color, and triturate the whole to a uniform mass.

If, however, the aniline color is to be used in solution, dissolve it in the smallest possible quantity of alcohol, and very gradually add to this solution the glycerin and gum-arabic solution. It is also recommended to substitute sugar for one-quarter to one-third of the gum-arabic used.

Soluble stamping colors.—Since the introduction of readily-soluble aniline colors, the preparation of excellent stamping inks has been very much simplified. Water-soluble aniline blue is best adapted for the purpose. The ink is prepared by triturating the coloring matter with sufficient glycerin to form a mass of the consistency of syrup, which is spread by means of a brush upon a soft, smooth piece of cloth, and uniformly distributed with a small piece of wood.

The consistency of the stamping inks has to be varied according to whether they are to be used upon stamping

cushions, or for supplying self-inking stamps. For the stamping cushion—a piece of cloth which rests upon an elastic basis and upon which the ink is spread—thicklyfluid masses are most suitable, so that when the stamp is pressed against the cushion enough of the color adheres to it to yield a good impression.

For self-inking stamps, which are so arranged that the ink reaches the lower surface of the stamp through a piece of cloth, the ink must be more thinly-fluid, so as to permit it to penetrate the cloth with sufficient rapidity to allow of several impressions being taken in succession.

E. Dieterich gives the following formula for stamping inks for rubber stamps :---

Blue rubber stamp ink.—Water-soluble aniline blue 1 B 3 parts, distilled water 10, pyroligneous acid 10, alcohol 10, glycerin 70.

Mix the ingredients intimately by trituration in a mortar. The blue should be well rubbed down with the water, and the glycerin gradually added. When solution is effected, the other ingredients are added.

Other colors are produced by substituting for the blue any of the following :—

Methyl violet 3 B 3 parts; Diamond fuchsin I 2 parts; Methyl green, yellowish, 4 parts; Vesuvin B (brown) 5 parts; Nigrosin W (blue-black) 4 parts.

If a bright-red ink is required, 3 parts of eosin BBN are used, but the pyroligneous acid is omitted, as this would destroy the cosin. Other aniline colors, when used for stamping ink, require to be acidulated.

Rubber stamp color according to Boettger.—Dissolve bleu de Lyons to saturation with the aid of heat in concentrated glycerin, add some Thenard's blue, and thicken the liquid with finely-powdered gum-arabic.

Indestructible stamping ink.—To manufacturers of woven goods, it is of importance to mark their goods so that the marking cannot be removed from the fabric by washing, bleaching, or dyeing.

Carbon being the only body which resists all chemical agents, it must form an ingredient of all indestructible stamping inks.

Ordinary printing ink is well adapted for the purpose, but since, on account of its rapid drying, it would adhere only to the surface of the fabric and might possibly be removed by abrasion, it is recommended to mix it with one-quarter its volume of good linsecd-oil varnish. Such ink deeply penetrates into the fabric, and is indestructible, all known bleaching agents leaving it unchanged. If the fabrics are dyed a dark color, the ink may possibly be covered, but in case it is desired to expose the marking to view, it is only necessary to immerse the marked portion in chlorine water or a very dilute mixture of hydrochloric and nitric acids, whereby every coloring matter—even indigo and aniline black—is destroyed, and the marking becomes visible.

Stencil ink for wood.—An excellent stencil ink for boxes and packing-cases may be made by mixing lampblack, fine clay, and gum-arabic together. The lampblack gives the color, the clay furnishes a body, and the gum-arabic an adhesive. Water will answer as a solvent, but lamp-black is so light that a few drops of vinegar or acid will facilitate its admixture with the other ingredients. Any good adhesive substance, such

as dextrin or gum tragacanth, may be found to answer as well as gum-arabic to bind the mixture.

Colored stencil ink.—Shellac 4 parts, borax 1. Dissolve in a small quantity of boiling water and dilute with hot water to the consistency of very thin syrup. To this add a sufficient quantity of logwood or Brazilwood extract or soluble aniline red, for red. For blue, add to the solution soluble Prussian blue or blue carmine.

# XXVIII.

## WASH-BLUE OR LAUNDRY-BLUE.

IN commerce, many blue bodies are found which are sold as wash-blue. Such bodies are *smalt*, Berlin or Prussian blue, in a solid as well as dissolved state, indigo sulphonic acid, and indigo-carmine.

It is evident that the liquid varieties of wash-blue which contain the coloring matter in the form of a solution are to be preferred to the insoluble pulverulent kinds, since they spread over the smallest fibre, while the solid bodies only adhere mechanically to certain portions of the fabric.

A. INSOLUBLE WASH-BLUE.—Smalt.—Under this name a blue glass occurs in commerce which is prepared by fusing partially-roasted cobalt ores with a mixture of powdered quartz and pearlash. A silicate of potash is thus formed, in which the cobalt oxide dissolves with the formation of a bright-blue color. The mass, while still hot, is thrown into water and ground to powder under granite stones. If smalt is to be used for laundry purposes, it has to be finely divided in starch-paste, it possessing no cementing power by itself. In commerce, wash-blue powder is found, which consists of an intimate mixture of smalt and starch, and has to be boiled in water to be used for bluing.

Berlin or Prussian blue.—The preparation of Berlin or Prussian blue has been previously referred to. In a dry state it is hard and brittle, much resembling in appearance the best indigo. The freshly-fractured surfaces have a beautiful copper-red lustre, similar to that produced by rubbing indigo with a hard body. The dark-colored varieties are also called *Paris* blue.

For laundry purposes, Berlin blue also can only be used in connection with starch or gum. It has the great disadvantage that linen repeatedly blued with it in the course of time loses its pure white color and assumes a yellowish tone. This is caused by the Berlin blue, which is an iron combination, being gradually destroyed by the lye used in washing, and ferric oxide is formed, which imparts to the linen the yellow color.

B. SOLUBLE WASH-BLUE.—Soluble Berlin or Prussian Blue.—For the preparation of wash-blue, soluble Berlin blue is made in exactly the same manner as previously described under blue inks. It has the advantage over solid Berlin blue that, being a dissolved body, it is capable of greater division, and can immediately be poured into the water without the necessity of using starch.

It has the same disadvantage as regards the yellowing of the linen as the solid Berlin blue, though in a somewhat less degree, because the oxalic acid used as a sol-

vent for Berlin blue exerts a dissolving effect upon the ferric oxide.

It may here be remarked that linen which has become yellow by ferric oxide may be whitened by placing it for 24 hours in a solution of 1 part crystallized oxalic acid in 1000 parts soft water. The same solution will also remove rust-stains from linen.

Indigo wash-blue.—The indigo combinations are without doubt the best preparations for laundry purposes, because they are readily soluble in water, do not attack the linen, and adhere very uniformly to it. The indigo preparations are used either in the form of indigo-sulphonic acid or indigo-carmine, the former only in a liquid form, and the latter either solid, in a pasty state, or as solution.

Indigo-sulphonic acid or dissolved indigo may be readily prepared as follows :---

Reduce the indigo to a fine powder, and thoroughly dry it; then bring it into a glass vessel, and for 1 part by weight of it pour over it 2 parts by weight of fuming sulphuric acid. The mass becomes strongly heated, and, after stirring with a glass rod, is allowed to stand for 12 hours.

It is then poured in a glass funnel, the lower end of which is closed by a cork of fibrous asbestos, and the solution allowed to drain off. The solution at first obtained is so saturated that it looks perfectly black. By the addition of water, the indigo-sulphonic acid contained between the particles of indigo which remain undissolved is displaced.

The residue in the funnel consists of undissolved

indigo. It is dried in a porcelain dish, and again used for the preparation of indigo sulphonic acid. It is important to use a considerable excess of indigo as compared with sulphuric acid, so as to be sure that the fluid contains only indigo sulphonie acid and no free sulphuric acid, as the latter would have a destructive effect on the linen. The solution of indigo sulphonic acid is brought into commerce either in a concentrated state, as the so-called *indigo wash-blue essence*, or in a dilute state, as *indigo wash-blue*. A few drops of the concentrated fluid suffice for bluing the water in a large washtub.

Indigo-carmine.—The manner of preparing indigocarmine has previously been described, and it is only necessary here to say a few words in regard to the form in which it is brought into commerce as wash-blue.

Indigo-carmine, as previously mentioned, forms a pasty mass, which can only be sold in pots. Though this is the most concentrated form in which it can be obtained, and a very small pot of it suffices for a very large quantity of linen, it is not liked by washer-women, because they are apt to take too much of it, and the linen will not be white, but blue.

Various qualities of indigo-carmine in solution are brought in commerce. The concentrated product, which contains but little water, and is frequently designated *indigo-carmine essence*, is prepared by carefully adding to the indigo-carmine sufficient water to form a thick solution, which appears, even in thin layers, almost black, and shows a dark-blue color when running down on the sides of the bottle.

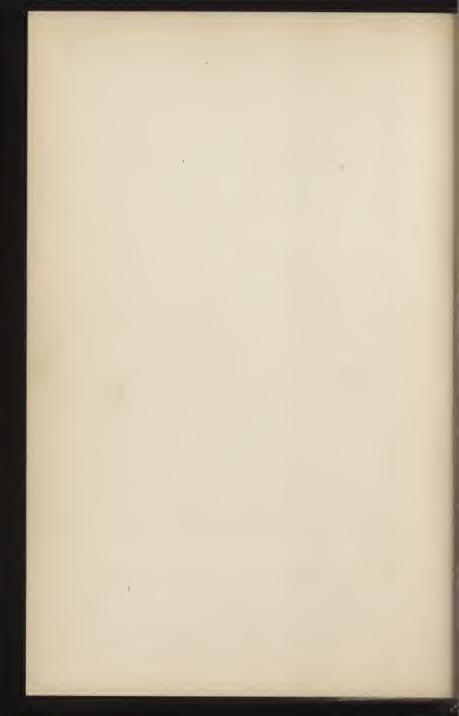
#### WASH-BLUE OR LAUNDRY-BLUE.

Indigo-carmine in solid form.—This product is prepared as follows :—

Indigo-carmine is triturated with sufficient potatostarch to form a thick paste, which, by kneading and pressing, is made as homogeneous as possible, and then pressed in moulds, resembling those used for moulding water-colors. The small tablets thus formed are removed from the moulds by gently knocking the latter against the table, and allowed to fall upon a sheet-iron plate. The latter is then placed on the top of an ordinary eooking-stove, and allowed to remain until the tablets have become hard, acquired a lustrous surface, and do not color the fingers when touched. It is still better to lay the sheet-iron plate eontaining the tablets upon a large shallow vessel in which water boils, thus avoiding the danger of overheating.

The purpose of heating is to eonvert the starch on the surface of the tablets into paste and to dry it, whereby a firm lustrous coating is formed. For use, break up the tablets and boil them in water, whereby the starch is ehanged to a paste of a deep-blue color, which can be readily divided in water.

Disinfecting wash-blue.—Mix together 16 parts of Prussian blue, 2 parts of carbolic acid, 1 part of borax, and 1 part of gum-arabic into a stiff dough. Roll it out into balls as large as hazel-nuts, and coat them with gelatine or gum to prevent the carbolic acid from escaping.



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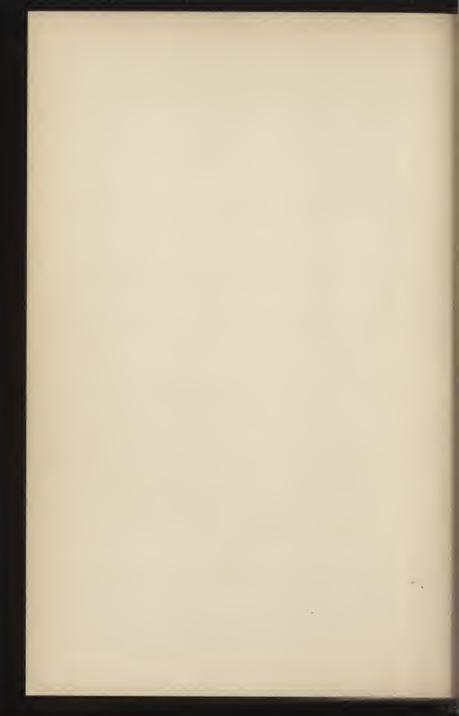
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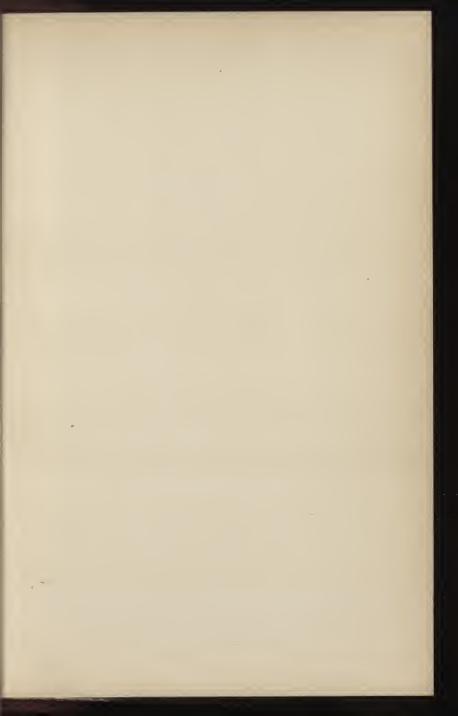
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