U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

INKS

CIRCULAR C413

U. S. DEPARTMENT OF COMMERCE
DANIEL C. ROPER, Secretary

NATIONAL BUREAU OF STANDARDS
LYMAN J. BRIGGS, Director

CIRCULAR OF THE NATIONAL BUREAU OF STANDARDS C413

INKS

By C. E. WATERS

[Issued December 28, 1936. Supersedes C400]

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1936

For sale by the Superintendent of Documents, Washington, D. C. - - - Price 10 cents

PREFACE

Since 1906, when the National Bureau of Standards began to test writing inks and a few other kinds, many hundreds of letters have been received from persons who wanted all sorts of information about inks. A printed circular can give a great deal more than would be feasible in a letter, so in 1920 Circular C95, Inks—Their Composition and Manufacture, was published. The second edition, in 1925, was called Inks, Typewriter Ribbons, and Carbon Paper. These gave almost no formulas, and because so many letters asked how to make inks, Circular C400, Inks, was written to try to satisfy this demand. Fifty or more formulas for a variety of inks were given in it. It was issued at the end of 1932 and since then has been in great demand, about 2,600 copies having been distributed.

The present Circular is a thoroughly revised and enlarged edition of Circular C400. It contains new formulas, and discusses subjects that were only briefly touched upon, if at all, before. It is believed that the present Circular is a distinct improvement on the one it supersedes.

Lyman J. Briggs, *Director.*

INKS

By C. E. Waters

ABSTRACT

This circular outlines briefly the history of writing inks, in particular those of the iron gallotannate type, gives formulas for a few of these inks and for three new iron gallate inks, discusses the aging of writing, the restoration of faded writing, and the effect of writing inks upon paper. After this, come brief discussions of several other kinds of inks, including colored writing inks, drawing, stamp-pad, recording, and other kinds. Formulas are given for most of them.

Printing inks and others that depend upon pigments for their color and their special properties are in a class by themselves, and little is said about them in this circular.

The methods of testing given in the Federal specifications for inks are described. Then follows an appendix in which are sections on weights and measures, on equipment for making ink in the home, and on dyes suitable for making inks. Finally, there is given a brief list of selected references.

CONTENTS

I. INTRODUCTION

Nobody can say how early in his long history man began to use signs and symbols to serve as reminders to himself, and to convey information to his fellows. No doubt the earliest of such signs were piles of stone, and the broken twigs we still use to mark an unfamiliar trail. The spirited though crude drawings left on the walls of European caves by men of earlier cultures than ours show that primitive man was akin to us. Worse art is to be seen today on walls in waiting rooms and other public places.

The walls of caves, flat rocks on the faces of cliffs, clay tablets, smooth slabs of wood, sheets of wax, and pieces of ivory, bone, and skin have all been used for writing upon. Even today a college diploma is a sheepskin in name if not in fact, and tattooing has not died out. For centuries parchment—the better kind is called vellum—was the material on which many books were written, and the papyrus roll was common enough to have given us the word "paper." Parchment and papyrus were expensive, and could not be obtained in large quantities, and there could have been no great development of printing, nor much letter writing, if the art of making paper from pulped vegetable fibers had not been invented.

We may never know when writing ink was first used, nor what it was made of. No doubt the juices of colored berries served as ink at a very early date, but it would be hopeless to look for samples of writing done with them. Dyes, whether made by nature or by man, have the unfortunate habit of fading. The same colored pigments that were stirred up with water to make war paint might also have been used for writing. The ink on the oldest manuscripts that have been found, which date from about 2500 B.C., was made with carbon, probably in the form of lampblack (soot) in most cases, though charcoal may have been used also. It is not known whether the lampblack was merely stirred with water and kept in this liquid form, or whether it was made into the sort of dry cakes we call chinese, or more often india, ink. These cakes, which have been in use for

3,000 years, are prepared by making lampblack into a stiff paste with a solution of glue, gelatin or "gum", (possibly gum arabic) in water, shaping the mass in molds, and drying it. When some ink is needed for writing, the end of a cake is rubbed with a little water in a shallow dish until enough of the dry ink to give the desired depth of color is dissolved.

Another much used kind of ink was sepia, a dark-brown secretion from cuttlefish, the same kind of animal that serves as food for man, in Europe, and provides the cuttle bone which hangs in the canary's cage.

Those who wish to read more about the history of writing are advised to consult books in public libraries. Two books that are suggested are by Mitchell and Hepworth,[1] and by Carvalho.[2]

II. IRON GALLOTANNATE AND GALLATE INKS

1. ANCIENT INKS

Leather tanned with bark was known before the Christian Era, and the staining of wet leather by contact with iron must have been noticed often. Yet the world waited for more than 2,000 years after the invention of india ink, or until about 1126 A.D., before tannin and iron were combined to make writing ink. This kind of ink is still used in larger quantities than any other. The ink was made by dissolving ferrous sulphate (copperas or green vitriol) and glue or gum in an infusion of nutgalls, which contain a kind of tannin that is especially suitable for making ink. The infusion of nutgalls was allowed to ferment, the other materials were added, and the mixture was left undisturbed for a time, so that solid impurities could settle out, and the solution could blacken. The change in color was caused by the action of oxygen from the air upon the iron salt. Ferrous iron forms with tannin an easily soluble compound that is not intensely colored, and oxygen converts this more or less completely into a ferric compound, which is black, and is nearly insoluble in water. Ink made by this process was a muddy fluid in which floated innumerable microscopic particles of the black compound. The glue or the plant gum helped to keep the particles from settling to the bottom of the fluid, and later served to fasten them to the paper or parchment.

In the early days there was no thought of chemical control of the manufacturing process, nor any chemist who could have supervised it. Not until 1748, when William Lewis began to experiment, was any attempt made to produce a "balanced" ink, with nearly correct proportions of iron and nutgalls; and even in his time there were no analytical methods to help him. Though he had to work by the cut-and-try method, he tried.

Because each ink maker used the formula he considered the best, but had no idea of the amount of tannin in the galls, nor of the purity of his ferrous sulphate, many a batch of ink must have been far from balanced in chemical composition. This state of affairs is reflected in the condition of old documents preserved in libraries in Europe. More about this will be found on page 20.

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[1] C. A. Mitchell and T. C. Hepworth, Inks, Their Composition and Manufacture, 3d ed. (Chas. Griffin & Co. (Ltd.), London, 1924.)

[2] D. N. Carvalho, Forty Centuries of Ink. (The Banks Law Publishing Co., New York, 1904.)

2. MODERN INKS

About the middle of the nineteenth century a change was made in the manufacture of writing ink. Instead of deliberately letting it oxidize and be turned into a muddy fluid, it was guarded from the action of the air and kept clear as long as possible. When a batch of ink is made nowadays, it is allowed to remain undisturbed for a time so that solid impurities will settle to the bottom, but only a small part of the iron salts in a vat containing some hundreds of gallons of ink will become oxidized.

The coloring matter of the older inks consisted of black particles that remained to a great extent upon the surface of the paper. The modern clear inks soak into the fibers of the paper, or penetrate between them, and then become oxidized. For this reason it can be argued that the clear inks should be the more permanent, because so little of the writing is on the surface, where it can be rubbed off. To keep the ink clear as long as possible, it must be kept from oxidation, and must also contain a small quantity of free acid, usually hydrochloric or sulphuric acid, to hold in solution the black iron compound whose formation can not be avoided entirely. The more free acid the ink contains, the longer will it remain clear, but the greater will be its destructive effect upon paper, and its corrosive action on steel pens. There must be some sort of compromise if the use of iron gallotannate ink is not to be abandoned. Our ancestors two or three generations back were not concerned with the acidity of their ink. It was muddy anyhow, and they had no steel pens to be corroded. The fountain pen with its noncorrodible point puts a temptation in the path of the ink maker, who knows what an extra amount of acid will do for him in keeping the ink clear.

Ink which has undergone but little oxidation does not look intensely black in the bottle, and the marks it makes on paper are so pale at first that it is necessary to give the ink a stronger color by the addition of a dye. The dye would not be needed if letters could always be kept for a day or two for them to become easier to read. When clear gallotannate inks began to be made, the synthetic or so-called aniline dyes were something yet to be discovered. Of the comparatively few dyes available in those days, it is probable that only indigo could have been used without causing the precipitation of solid matter in the ink. Indigo itself is not soluble, but by suitable treatment with strong sulphuric acid it is converted into the disulphonic acid, which dissolves readily and forms no precipitate by combining with the other ingredients of the ink.

3. A DEFINITION OF INK

In 1890, Schluttig and Neumann, ink chemists of Dresden, Germany, wrote what is in many respects the most important book on iron gallotannate inks, because of its far-reaching and lasting influence.[3] Their definition of ink, their explicit recommendations for making record ink, and the whole tone and spirit of the book set a new mark for the ink maker to aim at. As a basis for some of the discussion in the pages which follow, their definition, in nearly literal translation, is here given.

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[3] O. Schluttig, and G. S. Neumann, Die Eisengallustinten (The Iron-Gall Inks), (v. Zahn & Jaensch, Dresden, 1890).

By ink we mean a liquid, suitable for writing, which

1. Is a clear, filterable solution, not a suspension;
2. Is mobile and keeps for a considerable time; that is, it flows easily from the pen, and neither clogs, drops off, nor spreads on the paper;
3. Has good keeping quality in glass; that is, in the inkstand it forms
   (a) A slight deposit only slowly,
   (b) No skin-like deposit, on the surface or on the walls, and never any mold;
4. On a good pen it forms only a slight, varnish-like, smooth coating, but not a loose, crusted one;
5. Has no pronounced odor;
6. Is not too acid and does not penetrate through good paper;
7. Has an intense color, which does not become paler nor bleach out entirely in the liquid or on paper (in the latter case judged after the complete drying of the writing, for moist lines always look darker than dry ones);
8. Gives writing that is not sticky after drying.

Every good ink, whether writing, or combined writing and copying, should have these qualities. There is no sharp boundary between the two kinds, but if the ink is intended only for writing, it should in addition:

9. Give writing that, after drying for eight days, is not removed by water or alcohol—even by treatment for days—to such an extent that it becomes illegible.

Finally, if the ink is intended for imperishable records, it must have:

10. A definite minimum content of iron,
11. And enough tannin; that is, it must give writing which after drying becomes deep black within eight days, and which, even after treatment for days with water and alcohol, still retains a certain degree of blackness.

All the points in this curious definition are important, but not equally so. The authors stressed 1, 3, 6, 10, and 11. No. 10, of course, means not less than a definite minimum content of iron. In the work described in their book they tried to make ink that met the requirements of their definition to the fullest possible degree. Taking it for granted that the ink should contain iron, they first studied the effect of having different amounts of that metal and of gallic and tannic acids in the solution. Having done their best with these materials, they extended their investigation to include inks made with iron and substances that are closely related to gallic acid in their chemical structure. Their conclusions may be better understood after reading a short discussion of gallic and tannic acids.

4. THE TANNIN IN IRON GALLOTANNATE INKS

The tannins are a group of more or less closely related chemical compounds that are found in many different kinds of plants. Their name comes from the use of some of them for tanning the skins of animals to make leather. The chemistry of this group of substances is quite complicated, but a good start has been made in determining the molecular structure of the tannins. It has been proved that many of them are glucosides, or compounds of the familiar sugar, glucose (dextrose), with the various organic acids that are the real tanning agents. Chemically, glucose is an alcohol, and its compounds with these acids are esters, or salts, as truly as ethyl acetate is the ester, or salt, of ethyl alcohol and acetic acid. Under suitable conditions, ethyl alcohol and acetic acid react as shown by the following equation, to produce ethyl acetate and water. The atoms that presumably unite to form water are in italics.

$$\underset{\text{acetic acid}}{CH_3CO.\mathit{OH}} + \underset{\text{ethyl alcohol}}{(\mathit{H}O)C_2H_5} = \underset{\text{ethyl acetate}}{CH_3CO.OC_2H_5} + \underset{\text{water}}{H_2O}$$

If ethyl acetate is heated with water, the reverse reaction takes place to some extent, and ethyl alcohol and acetic acid are recovered, as shown by reading the equation from right to left. The ethyl acetate can be broken down completely into alcohol and acid if some caustic soda is dissolved in the water, but in this case sodium acetate, and not the free acid, is obtained. This is a typical example of "hydrolysis", or the splitting of a compound by its combining chemically with water. By an exactly similar reaction the natural tannins that are glucosides can be split into glucose and organic acids.

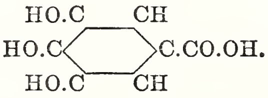
As already said, glucose, $C_6H_{12}O_6$, is an alcohol, but it differs from ethyl alcohol in being able to combine with five molecules of acid, instead of with only one. This difference can be indicated by writing the formula of glucose thus: $(HO)_5C_6H_7O$. Then if RCO.OH represents any one of the numerous acids that occur in the tannins, its glucoside may perhaps be formed in the plant by the following reaction, which has been brought about in the chemical laboratory:

$$\underset{\text{"tannic" acid}}{5\mathrm{RCO.}\mathit{OH}} + \underset{\text{glucose}}{(\mathit{H}\mathrm{O})_5\mathrm{C_6H_7O}} = \underset{\text{glucoside}}{(\mathrm{RCO.O})_5\mathrm{C_6H_7O}} + \underset{\text{water}}{5\mathrm{H_2O}}$$

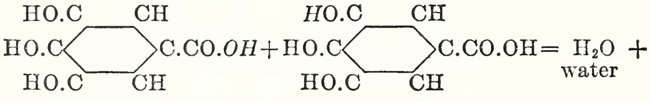
As before, the atoms that unite to form water are in italics. The equation when read from right to left expresses the hydrolysis of the glucoside into acid and glucose.

The best known of the natural tannins is the glucoside of tannic acid, which is also called gallotannic acid, digallic acid, gallylgallic acid, or simply tannin. Three of these indicate a relationship to gallic acid, which gets its name from the ultimate source, nutgalls.

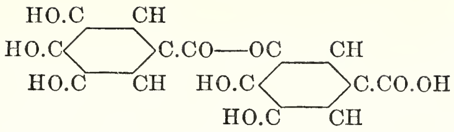
To the organic chemist, gallic acid is 3, 4, 5–trihydroxybenzoic acid, which means that it is benzoic acid, $C_6H_5CO.OH$, in which the hydrogen atoms in the 3, 4, and 5 positions with respect to the carboxyl group, CO.OH, are replaced by hydroxyl, OH. Because it is a derivative of benzene, the structural formula of gallic acid is



The formula can also for convenience be written as $(HO)_3C_6H_2CO.$-OH, or for the present discussion as $(HO)(HO)_2C_6H_2CO.OH$. Gallic acid is thus both an acid, on account of the carboxyl, and an alcohol, because of the hydroxyl groups. Just as ethyl alcohol and acetic acid combine to form an ester, so two molecules of gallic acid can react to form an ester, in this case tannic acid. The equation makes this clear:



Two molecules of gallic acid



Tannic acid

It will be seen that tannic acid has a carboxyl group, so it can form salts or esters, including those known as glucosides. Finally, because it is an ester, it can be hydrolyzed in the same way as ethyl acetate. The equation just given, when read from right to left, shows how tannic acid takes up water and is hydrolyzed into two molecules of gallic acid.

Return now to the last two sentences of section 3. In addition to critically studying inks containing different amounts and proportions of gallic and tannic acids, Schluttig and Neumann made inks with 26 other substances that are chemically related to these two acids, but differ from them in the number and arrangement of the hydroxyl and carboxyl groups attached to the benzene ring, or that have methoxyl, OCH_3, groups instead of hydroxyl. Their conclusion was that in order to make ink of good color and permanence, the "tannin" must have three adjacent, free hydroxyl groups. This condition is satisfied by tannic acid and gallic acids, and these of all the substances studied were the best for making ink. Thus a formula probably discovered by accident, and improved empirically during the centuries, was shown to be scientifically correct, so far as an essential part of it is concerned.

5. FORMULAS FOR IRON GALLOTANNATE AND GALLATE INKS

(a) HISTORY OF FORMULA FOR GOVERNMENT RECORD INK

It does not suffice to find the best materials for making ink, because unless they are used in the correct amounts, the ink will not be good. There should be no excess of either iron salt or of tannin, the amount of free mineral acid should be just enough to keep the ink clear for a reasonably long time in the bottle, and there must not be a deficiency nor an excess of dye. The formula for "copying and record" ink given on page 9 of this circular differs in but two respects from the one recommended by Schluttig and Neumann, as the result of their long investigation. They used 10 grams (hereafter written "g") of gum arabic, the "acacia" of the U. S. Pharmacopœia, in a liter of ink, to act as a preservative, as they put it. As we would now say, it served as a "protective colloid" to hinder the precipitation of any insoluble ferric gallotannate formed in the ink. Some years ago the gum was omitted from the United States Government formula when proposals for bids were being typewritten. This clerical error was discovered too late to be corrected, because the contract for a year's supply of ink had been awarded. This led the then Bureau of Chemistry, U. S. Department of Agriculture, to make special tests of the ink with and without gum arabic. These tests showed that the omission of the gum was an improvement, and ever since then the gum has been left out of the formula for the standard ink.

The Government formula calls for a dye that is different from the one recommended by Schluttig and Neumann, though the two are closely related in composition. This is further discussed on page 51.

In the early 1890's, the Commonwealth of Massachusetts adopted the Schluttig and Neumann formula as the official ink for records and other public documents. A few years later the Federal Government started to use it, and about 1914 Connecticut followed their lead. It should be noted that Prussia, in 1912, decreed that the official ink should contain at least 4, and not more than 6, g of iron in a liter, these being the limits set by Schluttig and Neumann for record ink. In this country the maximum, 6 g of iron, has always been required. This weight of the metal is contained in the 30 g of ferrous sulphate crystals in the formula. Massachusetts requires 10 g of gum arabic in a liter of ink, but curiously enough is silent about the use of blue dye.

(b) STANDARD FOR GOVERNMENT COPYING AND RECORD INK

In 1924, the Federal Specifications Board took over the old specification for "Treasury Standard" writing ink, and promulgated it as United States Government Master Specification 163, Record and Copying Ink. It was published as Circular C182 of the National Bureau of Standards, which went out of print in 1930. Although it is not a true copying ink, it will give one good press copy when the writing is fresh, and this generally suffices. In 1930, the specification was changed in form, but not in technical requirements, and issued as Federal Specification TT–I–521, Ink; Copying and Record, a part of the Federal Stock Catalog. The apparent subordination of "record" to "copying" is the result of alphabetical exigencies, so that the specification will fit into its proper place in the catalog.

Like other specifications for inks, this one gives a formula for making ink to be used as a standard for comparison when testing samples of inks bought by the Government. Many who read the specification labor under the mistaken impression that the manufacturer must use the same pure materials for producing the ink he furnishes. This idea is not in accord with the wording or the intent of the specification. It is necessary, in order that both buyer and seller shall be able to test the ink on the same basis, that the standard ink shall be made of chemicals of definite purity. Any manufacturer who has the knowledge and skill to use cheaper raw materials in making ink that meets the requirements of the specification, may do so.

A standard ink is necessary because some of the requirements of the specification can not be stated in exact terms, and because some of the properties of the ink that are measured by the tests may differ according to the conditions under which the tests are made. If the standard and the sample are put through the same series of tests, side by side, it is easy to see whether the sample is equal to the standard in all essentials.

In the following formula for the standard copying and record ink of Federal Specification TT–I–521, all the materials must be "of the strength and quality prescribed in the edition of the United States Pharmacopœia which is current at the time bids are asked for." This, however, does not apply to the dye.

Standard Copying and Record Ink

	Grams
Tannic acid	23. 4
Gallic acid crystals	7. 7
Ferrous sulphate crystals	30. 0
Hydrochloric acid, "dilute", U.S.P	25. 0
Carbolic acid (phenol)	1. 0
Soluble blue (C.I. 707; Sch. 539)[4]	3. 5
Water to make a volume of 1 liter at 20° C (68° F).	

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[4] The symbols in parenthesis, here and throughout the circular, indicate definitely the dye type intended. See explanation on p. 49.

The temperature at which the volume is made equal to 1 liter is, for practical purposes, of no importance. This applies also to the next two formulas.

(c) FORMER STANDARD FOR GOVERNMENT COPYING INK

There is no Federal specification for true copying ink. Years ago fairly large quantities of "Treasury Standard" copying ink were bought on a specification based on the following formula:

Standard copying ink

	Grams
Tannic acid	46. 8
Gallic acid crystals	15. 4
Ferrous sulphate crystals	60. 0
Hydrochloric acid, "dilute", U.S.P	50. 0
Gum arabic (acacia, U.S.P.)	10. 0
Carbolic acid (phenol)	1. 0
Soluble blue dye [5]	5. 0
Water to make a volume of 1 liter at 20° C (68° F).	

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[5] In those days, the dye was expected to be bavarian blue *DSF*, which was recommended by Schluttig and Neumann. See also p. 52.

As in the preceding formula, and in the one which follows, all the ingredients except the dye are to be of the strength and quality prescribed in the current United States Pharmacopœia.

To make the writing transfer more readily in a letterpress, some copying inks are made with the further addition of dextrin, sugar, glycerol (glycerin), or other similar substance. If too much is used, the writing will be sticky.

(d) STANDARD FOR GOVERNMENT WRITING INK

The copying and writing ink is of too heavy a body to please most writers, so there is a Federal Specification, TT–I–563, Ink; Writing. It was written originally to provide ink for use in post-office lobbies, where the conditions are devastating to pens. The standard ink of this specification is similar to some of the commercial writing inks. Except for the amounts of dye and preservative (carbolic acid), it is half as concentrated as the copying and record ink. The effectiveness of the preservative depends upon the quantity of it in a given volume of solution, and the ink must contain only enough dye to give a good color to the fresh writing. So the weights of these two ingredients are the same as in the more concentrated ink. The formula for the standard writing ink is:

Standard Writing Ink

	Grams
Tannic acid	11. 7
Gallic acid crystals	3. 8
Ferrous sulphate crystals	15. 0
Hydrochloric acid, "dilute", U.S.P	12. 5
Carbolic acid (phenol)	1. 0
Dye (C.I. 707; Sch. 539)	3. 5
Water to make a volume of 1 liter at 20° C (68° F).	

It is hardly necessary to say that the materials for making this ink must be of the same quality as those for making the other standard iron gallotannate inks.

(1) *Concentrated Ink.*—Concentrated ink is accepted if it meets the requirements of the specification for writing ink. The contents of the usual small bottle or the collapsible tube in which the ink is packed will make a quart of writing fluid when mixed with water. Hydrochloric acid is a solution of a gas in water, and it is therefore volatile. For this reason it is probable that most producers of concentrated ink use an equivalent amount of sulphuric acid instead, because for all practical purposes it is nonvolatile.

Concentrated ink occupies less space and weighs less than its equivalent in writing fluid, so the bottle is not so apt to be broken in shipment as a quart bottle of fluid, to say nothing of the saving in express or postal charges. It is also less apt to freeze and burst the bottles than the more dilute writing fluids; while if breakage should occur, surrounding packages will suffer less harm.

(2) *Ink Powders and Tablets.*—Ink powders and tablets represent the last step in concentrating ink. At the time the Federal specification for writing ink was written, and for some years afterwards, the few samples of these kinds of ink that had been examined by the National Bureau of Standards consisted wholly of dyes, or else they were quite unsatisfactory mixtures that purported to make good iron gallotannate inks. It is needless to point out their faults in detail.

The chief problem to be solved in making an ink powder—a tablet is only the compressed powder—is to find a dry acid that will fully take the place of hydrochloric or sulphuric acid. This problem was solved in 1931 by one manufacturer, whose product has been tested numerous times by the Bureau, though never completely analyzed. Since then a chemist of the Bureau has developed two formulas for ink powder, that are given in the next section.

(c) IRON GALLATE INKS

With the primary object of making an ink powder that will produce writing fluid of good keeping quality, low acidity, and satisfactory permanence, a great number and variety of formulas were systematically studied by one of the chemists of the Bureau.[6] It was found that ink will keep longer without depositing sediment if it is made without tannic acid, but with an increased amount of gallic acid. It was also found possible to replace the usual hydrochloric or sulphuric acid by less than an equivalent quantity of a solid organic acid. Two of the formulas in this section will make ink powders that can be kept in the dry state for a long time, and that produce unusually stable writing fluid, provided dye of the right quality is used. This is discussed in detail further along in this section.

The first of the two formulas for ink powder is a departure from custom, in that it requires ferric sulphate instead of ferrous sulphate. The weights of the ingredients needed to make a liter of writing fluid are:

Ferric Sulphate Ink Powder

	Grams
Gallic acid crystals	10. 0
Ferric sulphate, anhydrous	10. 7
Oxalic acid crystals	2. 0
Soluble blue (C.I. 707; Sch. 539))	3. 5

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[6] E. W. Zimmerman, *Iron gallate inks—liquid and powder.* J. Research NBS **15**, 35–40 (1935) RP807.

The weight of ferric sulphate called for, 10.7 g, contains 3 g of iron. An equivalent amount of the hydrous salt can be used instead. The simplest plan is to determine the iron content of the ferric sulphate and from this to calculate the weight of the salt that will give 3 g of iron. Ink made by this formula does not corrode steel pens excessively, but it forms on them a thin, yellowish coating of ferrous oxalate.

A formula that makes a still better ink powder than the preceding is:

Ferrous Sulphate Ink Powder

	Grams
Gallic acid crystals	10. 0
Ferrous sulphate crystals	15. 0
Tartaric acid	1. 0
Soluble blue (C.I. 707; Sch. 539)	3. 5

As with the first formula, the ingredients are to be dissolved in enough water to make a total volume of 1 liter, and this will contain 3 g of iron.[7]

It was pointed out in the first paragraph of this section that the two formulas for powder will make ink that keeps well in the bottle, provided dye of satisfactory quality is used. Certain adverse comments by manufacturers led to the suspicion that the premature deposition of sediment that they complained about might be caused by the dye. Accordingly 10 lots of ink were made, by the second formula, that differed only in that each contained soluble blue from a different manufacturer, or 2 grades from a single manufacturer. During the 2 weeks of the usual sediment test (see p. 42), five of the inks deposited from a slight amount to a great deal of sediment. The other five inks stayed clear, and in this respect were superior to the standard writing ink of the Federal specification. The formation of sediment is caused chiefly by the action of atmospheric oxygen, so if it is kept in a bottle that contains a great deal of air above it, ink will sometimes become turbid in a week or two. The more air and the less ink in the bottle, the sooner will sediment be formed. A sample of ink made by the second formula, and containing dye that was known to be satisfactory for the standard ink of the specification, was kept in a half-filled bottle for 8 months before any sediment could be seen in it.

Strange to say, a solution that contains all the ingredients of the second formula except the dye is less stable, and becomes cloudy within a week. The reason for this is not known, but the actual fact has been checked a number of times with materials from different sources. It may be that the dye molecule itself acts as an antioxidant and retards the formation of sediment; or that the presence or absence of some impurity determines the rate of oxidation. On the other hand it is possible that the dye or an impurity in it acts as a "protective colloid", and delays the flocculation and precipitation of the colloidal particles of iron gallate in the solution.

The third of the new formulas does not make ink powder, because in it sulphuric acid is used instead of tartaric acid. For this reason it could be used for concentrated ink, especially because of the small volume of concentrated sulphuric acid required. Although not so

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[7] A patent based upon this formula has been applied for. If granted, it will be assigned to the U. S. Government.

named in the original publication, the following formula may be called:

Concentrated Writing Ink

	Grams
Gallic acid crystals	10. 0
Ferrous sulphate crystals	15. 0
Sulphuric acid (calculated as anhydrous)	0. 654
Soluble blue (C.I. 707; Sch. 539)	3. 5

Water to make a pasty mass or, for making writing fluid directly, enough water to make the total volume 1 liter.

Anhydrous sulphuric acid is so nearly impossible to obtain and to keep that 0.69 g (0.654/0.95) of the familiar 95-percent acid can be substituted in the formula. One milliliter of acid of this concentration weighs 1.84 g, so 0.69 g will be 0.37 ml. A liter of the standard iron gallotannate writing ink of the Federal specification contains 1.25 g of hydrochloric acid gas, equivalent to 1.77 g, or 0.96 ml, of 95-percent sulphuric acid. The use of only 0.69 g of this corrosive acid is greatly to the advantage of the new formula.

It is unfortunate that gallic acid is so little soluble that the formulas in this section can not be modified for making record ink containing the required 6 g of iron in a liter. On this basis 20 g of gallic acid would have to be dissolved in a liter. At 25° C (77° F) a liter of water will dissolve only 12.0 g of gallic acid, and still less at lower temperatures. The presence of the iron salt definitely increases the solubility of gallic acid, but not sufficiently. It has been found that at 25° C ink containing between 17 and 18 g of gallic acid in 1 liter can be made.

6. PREPARATION OF IRON GALLOTANNATE AND GALLATE INKS

In the formulas already given, and elsewhere in this circular, when water is called for it is to be understood that distilled water is best, with rainwater the second choice. There are parts of the country where the water of streams and wells is so hard, because of the calcium carbonate dissolved in it, that a substantial part of the acid in iron gallotannate and gallate inks will be neutralized if natural water is used for making them. Water that contains 300 parts per million of calcium, calculated as the carbonate, or 0.3 g in a liter, is not unknown. This quantity of "lime" will neutralize nearly 2.2 g, or almost one-eleventh, of the 25.0 g of dilute (10-percent) hydrochloric acid in a liter of copying and record ink. As the quantity of free acid is cut to a minimum in the formula, it is evident that the quality of the ink will suffer, if so much of the acid is neutralized. Writing ink contains only half as much acid as the other, so the hard water will neutralize almost 28 percent of the free mineral acid. Water that has been softened by the zeolite, or base exchange, process is as alkaline as before this treatment, and will neutralize as much of the acid.

To make a liter of one of the gallotannate inks for which formulas are given, dissolve the gallic and tannic acids in about 600 ml of water at about 50° C (122° F). For convenience, this can be done in a 1-liter measuring flask set in a vessel of warm water. As it may be necessary to heat the water, the flask must not rest directly on the bottom of the outer vessel, or it may be cracked by the heat. Stand the flask on a flat coil of heavy wire or on some other device that will keep it from actual contact with the heated bottom of the outer vessel.

Swirl the flask frequently to hasten the dissolving of the acids. Then add the requisite amount of hydrochloric acid, and the crystals of ferrous sulphate, which will soon dissolve. The flask and contents should then be allowed to cool to the temperature for which it is calibrated, preferably 20° C (68° F). Meantime dissolve the dye in a separate portion of 250 ml of water, and filter the solution directly into the measuring flask. Rinse the vessel in which the dye was dissolved with two or three small portions of water, not more than 100 ml in all, and pour each portion through the filter paper to wash as much of the dye as possible into the flask. It may be noted in passing that the dye should be so completely soluble that, after the filter paper has been rinsed, there will be not more than a few solid particles left on it. When the solution in the flask is at the correct temperature, the carbolic acid can be added, and finally enough water to make the total volume 1 liter. The ink must now be mixed very thoroughly by inverting the stoppered flask a dozen or more times.

Essentially the same procedure is followed when making the iron gallate inks described in section II, 5(e).

Hydrochloric acid is a solution of a gas in water. The usual concentrated acid contains about 36 percent by weight of the gas, the rest being water. The Pharmacopœia defines "dilute" hydrochloric acid as containing not less than 9.5 nor more than 10.5 percent by weight of the gas. The plain intent is to make 10-percent acid, and directions for making it are given. There are reasons for suspecting that some who make ink by one of the formulas given in this circular do not understand how to prepare the dilute acid, and that they regard the concentrated acid as 100-percent. If, acting on this belief, they mix 10 parts by weight of the concentrated acid with 90 parts of water, they will have only 3.6-percent acid. The correct way is to mix 100 parts by weight of the concentrated acid with 260 parts by weight of water. The 360 parts of the mixture will contain 36 parts of hydrochloric acid gas, or 10 percent.

The same principle must be applied if the strong acid is of some other concentration than 36 percent. If it seems preferable to measure the acid and water instead of weighing them, the density of the acid must be taken into account. The density of the 36-percent acid is about 1.19. If 100 ml is taken, it will weigh 119 g, and will contain 42.8 g of hydrochloric acid gas, the last figure being 36 percent of 119. To get 10-percent acid, add 309 ml of water, which will weigh the same number of grams, for all practical purposes. This will give a total weight of 428 g, containing 42.8 g of hydrochloric acid gas.

Some manufacturers claim that sulphuric acid is better than hydrochloric. Certainly it is easier to handle, because there are no disagreeable fumes. One part by weight of hydrochloric acid gas is chemically equivalent to 1.345 parts of 100-percent sulphuric acid, or to 1.416 parts (1.345/0.95) by weight of the usual concentrated acid of 95-percent strength (66° Baumé; density 1.84). Hence, in the writing ink, the equivalent of 12.5 g of "dilute" hydrochloric acid containing 1.25 g of the gas is $1.25 \times 1.416 = 1.77$ g of ordinary concentrated sulphuric acid; or $1.77/1.84 = 0.95$ ml.

An ideal but quite impracticable way to keep iron inks is in glass globes hermetically sealed by melting the glass together. A sample of about 200 ml preserved in this way had only a little sediment in it after being kept for 9½ years. Ink is sold in bottles, and these should be nearly full, and the corks as perfect as possible, and not the inferior ones with numerous cavities through which air can get in to the ink. It is said to be best to keep the bottles in the dark.

In the appendix is a short discussion of dyes that can be used in iron gallotannate and gallate inks.

7. AMMONIUM AMMONIUMOXYFERRIGALLATE INK

An ink that is of no present commercial importance, yet which gained some prominence in the newspapers on account of the work described in section II,11, is a solution of ammonium ammoniumoxyferrigallate in water. In 1908, two Rumanian chemists published the results of their studies on iron-gall inks,[8] and among other things described the method of preparing this compound, and suggested using a 7- to 8-percent solution of it as writing ink.

To prepare the compound, dissolve 7.5 g of ferric chloride (presumably $FeCl_3.6H_2O$, though it is not so stated by the authors) and 7 g of gallic acid in 100 ml of water. Add 15 ml of concentrated ammonia water, and then 140 ml of strong ethyl alcohol. This precipitates the ammonium ammoniumoxyferrigallate, which is filtered off and washed, first with dilute alcohol and then with strong alcohol. The first washing with dilute alcohol is intended to remove most of the ammonium chloride formed in the reaction. This salt is nearly insoluble in strong alcohol. At this Bureau, the first washing was done with a mixture of 12 volumes of strong alcohol and 10 volumes of water; a second washing was with 20 volumes of alcohol mixed with 10 of water; while the final washing was with strong alcohol alone. The black mass that remains on the filter is dried in the air. It dissolves readily in cold water, with an intense blue-violet color. When this solution dries on paper it becomes insoluble in water in less than an hour, and black in a few hours.

Unless some less wasteful method of preparation can be devised, it is unlikely that the compound will ever be used for making commercial ink. The liquid filtered from the original precipitate is intensely black, and the wash-alcohol is strongly colored, so it is evident that a considerable proportion of the material is lost. In addition, the large volume of alcohol which must be used increases the cost. A few experiments made at the Bureau indicated the possibility of preparing the compound by dissolving ferric hydroxide in a solution of gallic acid, and adding ammonia water to this solution of ferric gallate. However, to make a large quantity of ferric hydroxide and to wash it free from salts is a very difficult task.

8. AGING OF WRITING

The behavior of iron inks on paper is so important that it deserves to be discussed in some detail.

The fresh writing is blue, except in the rare case of the ink containing a black, instead of the usual blue, dye. In a few hours the writing becomes perceptibly darker, because the ferrous salt in the ink has

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[8] T. Silbermann and H. Ozorovitz, Bul. soc. stiinte Bucuresti **17**, 43–57 (1908). The abstract in Chem. Zentrbl. **1908**, II, 1024, gives the method in sufficient detail. Mitchell and Hepworth (see p. 87–89 of the book cited in footnote 1) also abstract the article, but have transposed the formulas for the ammonium salt and the acid from which it is derived. In a footnote on p. 88, they refer to Zetsche's criticism of the work of Silbermann and Ozorovitz, but give the wrong volume and year of the journal in which the criticism appeared. The correct citation is Liebigs Ann. Chem. **435**, 233 (1924).

begun to be oxidized to black ferric gallotannate. Under ordinary conditions of diffused daylight the writing should attain its greatest intensity of color, a deep blue-black, in about a week. If the ink is unusually acid, the color develops more slowly. On the other hand, if the ink contains too little acid, or if the acid is neutralized by exposing the fresh writing to the fumes of ammonia, the blackening will be complete in a day or two.

The oxidation that causes the blackening does not cease abruptly when all the ferrous iron is converted into ferric iron, for the dye and the gallic and tannic acids are also subject to oxidation. In the course of time the dye will disappear. If this occurs before the two acids have been affected to any great extent, the writing will still be black, but no longer blue-black. This is normal for a well balanced ink. If the ink maker depended more upon dye than upon iron gallotannate, it does not seem impossible that the aging writing will never go through the true black stage, but that when all the dye is gone, a substantial part of the gallic and tannic acids will have gone with it, and then the writing will have a brownish color. It is certain that if the paper endures long enough, finally nothing will be left of the writing but rusty lines of ferric oxide.

It is natural to ask how long it takes for all this to happen to the writing, and the reader can draw his own conclusions after being told of some of the factors which influence the rate at which the ink ages on paper. First of all comes the ink itself. If it is truly a record ink, the writing ought to last for centuries if it is kept under proper conditions. Ordinary writing ink can not be expected to last as long as record ink, and if both are used in the same document, as when two persons sign it, each with his own fountain pen, one might draw the conclusion 20 or 30 years later, that one signature is much more recent than the other. If one of the inks was too dilute, and also contained too small a proportion of gallic and tannic acids for the amount of iron, the writing might become rusty in a comparatively few years. The fluidity of the ink and the absorptiveness of the paper influence the quantity of ink in the written characters, and thus play their part in the aging. If the writing was blotted instead of being allowed to dry naturally, the ink is handicapped at the start. An inspection of old notebooks, ledgers, and similar records is apt to disclose considerable differences in the appearance of writing of the same date and in the same hand. Such differences are outstanding in the notebooks and lecture notes discussed in section II, 9.

The appearance of the writing after a number of years have gone by will also depend upon how it has been kept. If it has been much exposed to light and has been in a damp place, the writing will look older than if it has been kept in a dry atmosphere and in the dark. Apparently the character of the paper is not to be disregarded. According to Schluttig and Neumann, fresh writing will darken much more rapidly on some kinds of paper than on others. It is not to be supposed that this hastening of the oxidation by the paper will cease in a short time. It seems more reasonable to think that the paper will continue to affect the ink over a period of years. If it does, then of two pieces of writing, identical in every respect except the kind of paper, one will age more quickly than the other.

9. DATING A DOCUMENT

Examiners of "questioned documents" base their conclusions as to the age of the writing to a considerable extent on its appearance. As explained in the preceding section, writing done with iron gallotannate ink of the modern type in the course of time undergoes an orderly series of changes of color. Usually blue at first, it begins to blacken in a short time and reaches its greatest depth of color, a blue-black, in the course of 2 weeks, more or less. The writing continues to be acted upon by the oxygen of the air, so that first the dye, and then the gallic and tannic acid compounds, are oxidized away. Finally ferric oxide—rust—is all that is left. How long it takes for all these changes depends on a number of factors, as explained in the preceding section.

In examining a document, the first step is to find out what kind of ink was used, by applying small drops of appropriate chemical reagents to selected parts of the individual letters. If it was an iron ink, the presence of blue dye is tested for. The ease with which certain reagents dissolve the dried ink is also determined. The results of these and other tests, together with whatever collateral evidence can be gathered, are depended upon by those who testify as to the age of a document, or the relative ages of two or more signatures, supposedly written at the same time, yet suspected of having been written at different times. Because of the many factors that influence the rate at which writing ages, the National Bureau of Standards has always declined to express any opinion, based upon tests of the ink, as to the age of any sample of writing. However, the Bureau was at one time practically forced to examine a number of samples of writing in order to get some idea of the length of time it takes for the blue dye to disappear. In connection with a case in court, a chemist of the Bureau tested the writing of three letters of disputed age, solely to find out what kind of ink had been used, whether iron gallotannate or a solution of a black dye. It turned out to be an iron ink, and in reporting this it was added that the blue dye could be detected. This was at once seized upon by two experts, who said that the presence of the dye proved that the letters could not be more than 15 years old, which was an important point at issue. That the dye will disappear within this time seems to be the general opinion, though some few of those who make a study of such matters think differently. The belief that all the dye will disappear within a limited number of years is expressed by Mitchell and Hepworth[9] in discussing the results of tests made by them on a number of bank checks of different ages. They say: "In abnormal cases, where an excessive amount of ink had been used, some diffusion of the blue pigment may occur even after the lapse of twelve years."

Statements such as these led to the examination of a large number of samples of writing, 116 in all, in laboratory notebooks at the National Bureau of Standards, in university lecture notes, and in legal papers.[10] The writing was variously dated from 1851 to 1918. The tests were made in 1933, so all the writing was 15 or more years old. It can not be said that the writing was abnormal, nor that an excessive amount of ink had been used. Indeed, because on a given page the writing varied from a deep black to a pale color, care was taken to

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[9] C. A. Mitchell and T. C. Hepworth, Inks, Their Composition and Manufacture, 3d ed. (Chas. Griffin & Co. (Ltd.), London, 1924), p. 182.

[10] What follows in this and the next 3 or 4 paragraphs is a summary of an article by C. E. Waters, *Blue dye as evidence of the age of writing*, Ind. Eng. Chem. **25**, 1034 (1933).

test a medium-dark character as well as an intensely black one on each page. So in nearly half of the tests, the writing contained less than a normal amount of ink. Although the writing of the lecture notes (1895–96) and in the notebooks (1904–18) was all in the same hand, many different lots of ink must have been used. Some had evidently been blotted, and some allowed to dry naturally; some was done with a moderately blunt pen, and some with a fine-pointed one. It can be fairly said that these samples can be regarded as writing picked at random, and that the results obtained with them can validly refute the statement that the blue dye disappears within 15 years.

The tests were made as follows: A small drop of distilled water was placed upon a selected stroke of a letter or numeral. After it had stood for 10 seconds, it was removed by pressing down upon it, with a finger tip, a small piece of white filter paper with a fairly smooth surface. After 10 seconds, the paper was removed and examined for signs of blue dye. In many of the 116 tests, the result was recorded as "none", and in a few as "doubtful." When there was blue dye on the filter paper, the amount was estimated on an arbitrary scale in four steps, "trace", "faint", "distinct", and "strong."

Of two tests made on writing dated 1881, one showed dye faintly and the other distinctly. Two tests of writing of 1879 were negative, while one test each, representing 1851, 1852, 1865, 1872, and 1874, gave stains varying from faintly to strongly rusty, with no trace of blue. Writing of 1883 gave a negative test, but that of 1886 still contained blue dye. Of 12 samples dated 1895 and 1896, all gave positive tests. It turned out that the dates 1901 to 1918, inclusive, had little or no connection with the results. If the testing had been limited to writing that was just 15 years old—1918—what the two experts said would have been upheld, because four samples of that year failed to show any sign of dye. Yet writing dated from 1901 to 1917 was found to stain the filter paper to all degrees of intensity, at random. Of the 116 tests, 60 gave positive evidence, though slight in many cases, while 56 were negative or doubtful. This and the scattering of the positive and negative tests over the years show conclusively that the presence or absence of dye is no dependable criterion of the age of writing done within 50 years.

The method used by Mitchell and Hepworth differed from that of the National Bureau of Standards. They treated the writing with a 5-percent solution of oxalic acid to dissolve the surface film of iron salt which, according to their belief, will not let the dye escape from writing that is several years old. Oxalic acid removes this film and lets the dye dissolve and diffuse into the drop of liquid. Because of the many positive results obtained by the filter-paper method, 31 samples of the writing already examined were tested by the procedure of Mitchell and Hepworth, but with distilled water instead of a solution of oxalic acid. A tiny drop of water was allowed to stand on the selected letter or numeral. In most cases a deep black one was chosen. As before, the writing of 1881 gave positive results when tested in two places, because the two drops of water were faintly colored blue. Four tests of writing dated 1886 were rated from trace to strong. The writing of 1895 showed no dye in six tests, while for 1896, four out of eight tests were negative. Two samples dated 1910 gave strong evidence of diffusion of dye within 25 seconds.

It is evident that more than half of these results fail to support the claim that all the dye disappears within 15 years. If so mild a reagent as distilled water could bring out such differences as those described in this section, one should be cautious about drawing inferences from the action of other chemicals upon writing of unknown age. It is not even safe to be too positive about the age of writing that has a rusty appearance, with little or no black iron gallotannate. The ink may have been so poorly balanced in composition, or the writing may have been kept under such unfavorable conditions as to give a false idea of the age of the document. Like other matters, any expression of opinion relating to the age of writing lends itself admirably to forensic disputation.

During the past few years, a new method for ascertaining the age of writing has received notice in technical and other journals. This is the so-called "chloride test," which is based upon the fact that nearly all writing ink contains hydrochloric acid or metal chlorides. The chlorides spread gradually from the dried ink marks, supposedly by means of the film of moisture on the fibers of the paper. The extent of the spreading is taken as a measure of the age of the writing. It will be clear to the reader that the rate at which the chlorides spread from the strokes of the writing will depend upon a number of factors, for instance, the humidity of the air, which influences the film of moisture, and the character of the paper. In making the test,[11] the writing is treated with dilute nitric acid, containing silver nitrate to convert the chlorides into silver chloride, which is relatively insoluble and remains on the paper where it is formed. The writing is also decolorized by treating it with a solution of a nitrite or of permanganate. After the excess of silver nitrate is washed out of the paper with dilute nitric acid, the silver chloride is reduced to silver by treatment with an alkaline solution of formaldehyde or with sodium hydrosulphite. Silver obtained in this way is so finely divided that it looks black, so there is formed by the last reaction a zone that is darkest next to the strokes of the writing, and gradually becomes paler until it blends with the color of the paper. Because paper contains chlorides, acquired in the process of manufacture or from handling, it will be more or less darkened all over when the chloride test is applied.

According to Cornish, Finn, and McLaughlin,[12] the chloride test is unreliable. The paper in which their work is described ends with a list of experts or manufacturers who "were unanimous that such a test could not determine the age of ink writing under normal conditions, and that there was no reliable method known to science whereby the age of ink writings on documents could be accurately determined."

The authors cited in footnote 11 also discuss the spreading of sulphates from the strokes of the writing into the paper, as another means of determining the age of the writing.

An account of some tests made with a bleaching agent (hydrogen peroxide) upon 7 samples of writing, 1 day, 6 months, and 1, 2, 6, 14, and 22 years old, was found in an unexpected place.[13] The writer said that in order to determine the age of writing by the rate at which it is attacked by bleaching agents, certain "precautions" must be observed:

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[11] O. Mezger, H. Rall, and W. Heess, Z. angew. Chem. 44, 645 (1931).

[12] R. E. Cornish, J. Finn, Jr. and W. McLaughlin, *Age of inks by the chloride test.* Ind. Eng. Chem. News Ed. 12, 315 (1934).

[13] Workshop Receipts 5, 88 (Spon & Chamberlain, New York, 1903). The article, *Ink*, is signed by R. Irvine.

1. The inks must be those known as ordinary writing inks, prepared from iron and chromium salts and galls.
2. Writing dried by means of blotting paper is naturally more easily removed than writing which is allowed to dry on the surface of the paper; and light writing is somewhat more easily removed than coarse and heavy writing.
3. The bleaching solution must be exceedingly dilute, otherwise the action is so rapid and powerful that both old and new writings are removed almost simultaneously.
4. The action must be carefully watched, so as not to be too long continued. Lastly, very old writing which has become brown by age, although it resists the action of weak solutions of bleaching powder and hydrogen peroxide, will show signs of giving way almost instantly when acted upon by dilute nitric, hydrochloric, and oxalic acids.

To put "precaution" 2 in other words, unless all the writing was exactly the same at the start, tests made upon it will not determine the relative ages of different parts of the writing. It must be evident that questioned documents must be taken as they come, whether or not the writing was blotted, and in spite of some of it being light, and some coarse.

10. RESTORATION OF FADED WRITING

The choice of iron gallotannate ink for records is generally based upon its long resistance to fading, when kept under proper conditions, and little thought seems to be given to another advantage it has over an ink that is only a solution of a dye. When a dye fades, it sometimes leaves literally nothing behind on the paper, and if traces of oxidation products remain, they can not be detected readily, if at all. When an iron ink fades, it leaves small quantities of iron oxide in the lines of the letters, and this makes it possible to restore the legibility of the writing.

The vapors of ammonium sulphide will change the ferric oxide into ferrous sulphide, mixed with "molecular" sulphur. The ferrous sulphide will be brown or black, according to the amount of it. Writing restored to legibility in this way does not last long, because the iron sulphide is oxidized to sulphate in a few days, and there may be bad aftereffects upon the paper.

A 2- or 3-percent solution of tannic acid will also blacken the ferric oxide. This is by far the best treatment, because it produces essentially the same black compound that was in the writing before it faded, and because neither a strong acid nor a metal salt is left in the paper. In addition, it has been found (see section II, 11) that tannic acid does not cause deterioration of paper, in an accelerated aging test.

Again, a slightly acidified solution of potassium ferrocyanide will change the ferric oxide into prussian blue. This is a very permanent color, but the salts left in the paper by the treatment may later cause trouble.

The tannic acid and the ferrocyanide solutions can be applied by means of a brush. Another way is in a letterpress, by placing cloths or pieces of white blotting paper moistened with the solution in contact with the faded writing, and keeping the whole under pressure for a few minutes. A disadvantage of any chemical treatment is that iron is found in practically everything. Paper and dust contain it, and if the document has been much handled, it will have a surface coating, containing iron, that comes from dirty hands. The chemicals that are applied are not selective in their action, so that the writing is restored as dark lines upon a less dark and unevenly colored background.

If a source of ultraviolet radiation is at hand, it is better to defer the application of chemicals until the effect of this radiation has been tried. Under the right conditions the iron oxide will glow with a phosphorescent light that can be photographed. It is thus possible to get an exact copy of the writing without running the risk of damaging the document permanently.

A number of years ago, when it was decided to place the Declaration of Independence on exhibition in the Library of Congress, the National Bureau of Standards was consulted about the advisability of intensifying the writing by chemical treatment. After serious consideration of the uncertainty of full success, and of the danger of the action of the chemicals upon the document, it was decided that it would be better not to tamper with it, at the risk of ruining it forever.

11. EFFECT OF WRITING INK UPON PAPER

As was said on an earlier page, the condition of old documents in European libraries shows that not all the inks with which they were written were balanced in chemical composition. According to what we read, some of the documents are in excellent condition, while others have suffered to a greater or less extent from the action of the ink upon the paper. In some cases, only the unwritten margins of the pages remain, for all the rest of the paper has fallen to pieces. It is generally believed that this destruction of the paper has been caused by an excess of sulphuric acid in the ink. It is well established that this acid makes paper brittle. The excess of acid may have come from carelessly made ferrous sulphate. Another explanation of the destruction of the paper is that it has been brought about by the iron oxide in the ink. This oxide is supposed to act as an "oxygen carrier" to cause the weakening of the paper, just as a rusty nail, which is coated with iron oxide, attacks wood.

The effects of 12 writing inks, of different kinds, upon 7 kinds of writing paper were studied by the Bureau. In addition, solutions of gallic, tannic, and hydrochloric acids and of ferrous sulphate, in various combinations, but in the same concentrations as in writing ink, were tested with one of the papers. The tests were made by drawing parallel lines of a definite width and equally spaced across one-half of each sheet of paper. The folding endurance of the uninked and the inked parts of the paper was determined before and after subjecting the paper to an accelerated aging test. This test consists in keeping the paper at 100° C (212° F) for 72 hours, and measuring any changes in the folding endurance, which gives the best indication of any weakening of the paper.

The details of the investigation must be obtained from the original article.[14] It will suffice to say here that all the inks tested increased the deterioration of the paper in the accelerated test. The least harmful ink was a solution of 20 g of ammonium ammoniumoxyferrigallate in 1 liter of water. In the aging test one of the papers, without ink, retained 72 percent of its original folding endurance. The same paper, with lines drawn with this ink, retained 68 percent of its folding

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[14] E. W. Zimmerman, C. G. Weber, and A. E. Kimberly, *Relation of ink to the preservation of written records*. J. Research NBS **14**, 463–468 (1935) RP779. A summary of this work is given by B. W. Scribner and A. E. Kimberly, on p. 24 of the Bureau's Miscellaneous Publication M144, Summary Report of Bureau of Standards Research on Preservation of Records. Both publications give numerous references.

endurance, in the aging test. This difference is practically negligible. The next best ink caused a drop to 58 percent of the original folding endurance. This second ink was made by dissolving 15 g of dialyzed prussian blue, without the aid of oxalic acid, in 1 liter of distilled water. A commercial "acid-proof" ink made by dissolving prussian blue with oxalic acid would certainly cause greater deterioration of paper than the ink made by the Bureau. Solutions containing tannic and gallic acids, or these two acids with hydrochloric, had no harmful effect upon the paper. Ferrous sulphate, either by itself or mixed with the acids, caused weakening of the paper. Hydrochloric acid is so volatile that it escapes from the paper before it can do any harm. It was not necessary to make a test with sulphuric acid, because it has long been established that it is extremely harmful to paper.

12. INK ERADICATORS

When writing is removed with a steel eraser or with one made of rubber containing an abrasive material, the surface of the paper suffers, and it is not easy to write again over the same spot. To avoid this, various ink eradicators, chemical solutions that dissolve blue-black ink from paper, have been devised. Whether they will also dissolve dye inks, which are taken up in the pages which follow, depends upon the chemical nature of both the dye and the eradicator. If the latter has a strong bleaching—usually oxidizing—action, it is more likely to remove dye inks than if it acts merely as a solvent.

A drawback to the use of chemicals to erase writing is their effect upon paper. At first, no harm appears, but some of the chemicals will always be left behind, and finally damage the paper. Usually a brownish spot appears where the eradicator was applied, and after a while the paper is found to be brittle. The damage may be lessened by washing the spot. When the erasure is complete, dry the spot with a blotter, and then apply one or two drops of pure water. After a few moments remove the water with a blotter, and repeat the operation once or twice. This will not completely remove the chemicals, but it will help to save the paper.

The usual two-solution eradicators consist of a solution of bleaching powder or of javelle water and a dilute acid. Either of the first two has a bleaching action, which is made more rapid by the action of acids.

Cartons of bleaching powder, or "chloride of lime", can be bought in drugstores. Javelle water is made by adding sodium carbonate (sal soda, washing soda) to a solution of chloride of lime. Because the directions for making it are always printed on the carton, they need not be given here. If the solution of bleaching powder is to be used for removing ink, it should be diluted with water, to the same total volume as when javelle water is made from it by adding a solution of soda. Either solution will bleach, but the action is more rapid if an acid is used with it. A 5-percent solution of acetic acid can be used. Strong vinegar contains about this percentage of the acid, but if any great quantity is needed, it will be cheaper to buy the commercial 28-percent acid. One volume of this with 4.5 volumes of water will make a mixture that contains almost exactly 5 percent of acetic acid.

Oxalic acid, a poisonous crystalline substance, will dissolve dried iron gallotannate ink. The small packages of "straw hat cleaner" sold in drugstores are apt to be of this acid. It should be dissolved in about 20 times its weight of water. Much safer is a mixture of equal weights of tartaric and citric acids, dissolved in about the same amount of water as for oxalic acid. Citric acid is what makes lemons sour, and lemon juice has long been employed in the home for removing iron rust from garments.

In Farmers' Bulletin 1474, Stain Removal from Fabrics: Home Methods, the Department of Agriculture tells how to remove the inevitable ink spots from clothing and other fabrics.

III. OTHER KINDS OF INK

1. CARBON INKS

(a) CARBON WRITING AND DRAWING INKS

Carbon cannot be bleached by any amount of exposure to intense light, and it resists attack by chemicals that will quickly destroy paper. If carbon could be dissolved in water, it would be ideal material for making black writing ink. India ink, which has already been mentioned briefly, is not a solution of carbon, but a suspension of it in water containing gum or glue. To those who write with a brush, it matters little if the carbon settles to the bottom of the saucer of ink, for it can be stirred up with each dip of the brush. Fortunately for those of us who must use carbon ink with a pen, we have learned how to keep the carbon from settling to the bottom.

If some purified lampblack is stirred with water and then left to itself, after a time it will settle and leave clear water above. If the mixture is ground a long time, and then allowed to stand undisturbed, the carbon will not settle so quickly as before, and part of it may be very slow, indeed, in reaching the bottom. If instead of pure water, a solution of some plant gum, of shellac and borax, or of soap is used, after thorough grinding the carbon will tend to remain in suspension a long time. The difficulty in preparing a permanent suspension of carbon lies in the grinding. If it is ideally complete, no two particles of carbon will touch one another, much less cling together, but each will be separate from all the others, and each will be coated with an adsorbed film of gum, shellac, or soap. The carbon will then have almost no tendency to settle. Microscopic examination shows that ordinary lampblack consists of clusters of extremely small particles. Grinding does not make these ultimate particles smaller, but separates them from one another.

Carbon black can now be obtained that disperses readily when stirred with water. It comes in the form of a stiff paste, which is probably made by grinding carbon black with a solution of gum or some other colloidal material.

The manufacturers of black drawing ink are very successful in making practically permanent suspensions of carbon. According to one manufacturer, the ink mixture is ground for 3 or 4 weeks in a ball mill. If this is necessary, it is a sufficient reason why carbon ink can not be made satisfactorily by hand grinding.

Water that is clouded by extremely fine particles of clay in suspension will clear quickly if some salt is dissolved in it. Similarly, the carbon in an ink will settle rapidly if some acid is added. Alkali, on the other hand, makes the suspension of carbon more stable. The ammonia that can be smelt in some drawing ink is a mild alkali.

Because of the sensitiveness of carbon suspensions to acids, carbon inks can not be mixed with iron gallotannate ink, and a fountain pen that has held the latter must be cleaned with extreme care before filling it with a carbon ink. Carbon inks might be popular if it were not so easy to ruin them by ignorance of their peculiarities, or by carelessness.

(b) PRINTING, CANCELING, AND OTHER CARBON INKS

Black drawing ink contains only a small percentage of solid matter, and it does not differ greatly from clear inks in fluidity and working qualities. Other kinds of carbon inks range in consistency from only slightly viscous fluids to stiff pastes, which may contain as much as 25 percent by weight of carbon. The carbon in a canceling ink should be carried into the paper, and remain there in spite of attempts to remove the marks by washing. Mimeograph and other duplicating-machine inks require great care in their formulation and manufacture. If the mimeograph ink is not made just right, the copies made with it may be too pale, because the carbon clogs the stencil, instead of passing through it readily. Again, the ink may go through the stencil too freely, and may become smeared over the face of the stencil, and from that to the paper.

Printing inks contain more carbon than any other kind of ink, and among themselves they differ widely. Some are thick liquids, and others stiff pastes, with all consistencies between. It is necessary to adapt the physical properties of the ink to the kind of printing to be done. The same ink can not give equally good results in printing from ordinary type, from a lithographic stone, a halftone cut, and an engraved plate; and the paper introduces another important factor in the results.

Formulas for various kinds of carbon inks are to be found in books, but they should be regarded as only suggestions. The character of the finished ink depends upon the physical and chemical properties of the ingredients, upon the amount of each that is used, and upon how the ink is made. The various commercial forms of carbon that are used as pigments differ among themselves in physical properties, and can not be used indiscriminately. There are no Federal specifications for any of these inks, because there are no laboratory tests that can take the place of actual trials on the press, and with the paper and the kind of work for which the ink has been made. The ink manufacturer has his working formulas, but he would not turn over the actual production to an unskilled person.

It is possible to measure some of the properties of some of the ingredients of a printing ink, but there is no way by which to predict exactly what the finished ink will be like. The consistency, for instance, depends to a great degree upon what is called the oil absorption of the pigments. This differs according to their chemical composition, and is closely tied up with the fineness and degree of dispersion of the pigment. The last is largely dependent upon the grinding.

The difficulties involved in the manufacture of a pigment ink are well illustrated in the description of the process by which the United States Government Printing Office makes mimeograph ink.[15]

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[15] Government Printing Office Tech. Bul. 15, Standard Mimeograph Ink and Paper.

2. DYE INKS FOR WRITING

As explained on an earlier page, when an iron ink fades with age, it leaves behind on the paper at least a little iron oxide, and thus it is possible to restore the writing to legibility by suitable chemical means. When the ink is merely a solution of a dye, there is no possibility of such a restoration when the writing fades. Oxidation of the dye forms volatile products which escape into the air, or maybe small amounts of other products which remain in the paper, but with which there is no certain, dependable way of forming colored compounds. For these reasons dye solutions are not regarded as suitable for record inks. On the other hand, they have advantages over iron inks. They keep almost indefinitely in the bottle, are seldom corrosive, and because they contain less solid matter than iron inks they do not form thick deposits if they dry on pen points. Besides, if a crust does form, from a dye ink, on an unwiped pen, it will usually redissolve when the pen is again dipped into the ink, something that does not happen to the incrustation from an iron ink. A liter of the standard writing ink of the Federal specification contains 35 g of nonvolatile solids, while the same volume of a dye ink may contain no more than 10 g of solids, and sometimes a great deal less. In Federal Specification TT–I–549, for red ink, the standard is made by dissolving only 5.5 g of crocein scarlet *3B* (C.I. 252; Sch. 227) in a volume of 1 liter. A still weaker solution of methyl violet *B* (C.I. 680; Sch. 515) would suffice for that color.

Although dye inks are not considered suitable for records, they are not to be condemned on that account. They are excellent for ordinary correspondence, and for writings that are not meant to be records of permanent value. If kept in a dry place, and away from the light, there is no reason why writing with dye ink should not last for many decades. In some of the oldest record books of the Post Office Department, dated before 1800, there is writing with red ink. It may have been bright red at first, but it is now brownish red, and of surprisingly good intensity. At the National Bureau of Standards is a book in which there are several press copies of letters written early in 1901. The inks represented are iron gallotannate, blue from a "copy blue" typewriter ribbon, violet from printing ink containing dye of that color, and another violet from rubber-stamp ink. There are also two red lines on a page with a rough drawing. Evidently the drawing was made on a scratch-pad, and when the sheet was torn off in order to make the press copy, a little of the red glue ("padding compound") that was on two edges of the pad, came with it. This was enough to make the two red lines in the press copy. A press copy contains only part of the coloring matter of the original, and it might be expected to fade quickly on that account. In spite of this, the copies are still of good color, 35 years after they were made, and there is nothing to suggest that they will not last as long again, if they are kept under the same favorable conditions as heretofore.

There are no Federal specifications for writing inks made of dyes of other colors than red. There are many water-soluble dyes, and it is possible to make inks of almost any shade and hue by dissolving suitable dyes in water. If it should turn out that a particular ink has a tendency to "feather", or make blurred spreading lines on paper, this can be prevented by dissolving in the ink some gum arabic, say 20 or 30 g in a liter. Another expedient will be found in the account of recording inks.

Many dyes have an antiseptic action, so their solutions do not become moldy, though no preservative is added to them. With other dyes it is necessary to use about 1 g of phenol or other preservative in a liter of ink. If a dye is just on the border line, the addition of gum arabic to the ink might encourage the growth of mold that would otherwise not thrive. No systematic work has been done on this subject by the Bureau. Anybody who is interested in a particular dye or dyes can easily test them for himself by inoculating the solution with mold spores and keeping it in a dark, warm place for about 2 weeks. It is sometimes noticed that mold will not grow on ink, but will do so on the cork of the bottle in which the ink is kept.

When a dye ink is used in a fountain pen, sometimes trouble is experienced by incrustations of dried dye on the point of the pen. This can be avoided by mixing with the ink about one-tenth its volume of glycerin, which retains enough moisture to keep the dye from separating in solid form. If much more glycerin is added to the ink, it will dry too slowly on paper, and for that reason the writing easily becomes smudged. Indeed, even if only one-tenth volume of glycerin is added, the first few words written with a fountain pen that has not been used for a few days may show by their slow drying that evaporation has caused a concentration of the glycerin at the pen point.

(a) WASHABLE INKS

Now and then somebody asks how to make washable ink. In the generally accepted sense, a washable ink is one that can not be removed by washing; in other words, it is indelible ink. The inquirers, however, use the word in exactly the opposite sense, for they want to make ink that can be washed out of fabrics easily and completely. No study has been made of this subject by the Bureau, but in theory, at least, it is easy to make such inks by selecting dyes that do not fix themselves upon the fabric except with the aid of a mordant. Mordants are substances that form insoluble compounds with the dyes, so they are much used in dyeing, in order to fix the colors more lastingly to the fabrics. If the fabric is made of cotton or other vegetable fiber, the direct, or substantive, dyes should be avoided for washable inks, because, as their name implies, they are taken up directly by the fabric without the aid of a mordant. If the fabric is silk or wool the problem is far more difficult, because these fibers can be colored by dyes of almost any class.

(b) QUICK-DRYING INKS

Another question that is sometimes asked is how to make writing ink dry more rapidly. Ink dries partly by evaporation and partly by soaking into the paper. Alcohol evaporates more rapidly than water, and also is absorbed more rapidly by paper. Good writing paper is sized with glue or rosin, to keep watery solutions that are either neutral or slightly acid from being absorbed so rapidly that they will spread too widely. In other words, the paper is sized in a way intended to keep ordinary writing inks from making blurred marks. A strongly alkaline ink would quickly show on the opposite side of the paper. The situation will be even worse if a large proportion of alcohol is added to the ink, which will then penetrate paper and even thin cards almost in an instant. The proportion of alcohol that can be added safely to a given volume of ink will depend upon the kind of ink and upon the paper as well. The results of a few experiments may be of interest. Starting with 10 volumes of ink, a measured volume of alcohol was added to it, and the mixture was then tested by writing and by drawing light, medium, and heavy lines with an ordinary pen upon scratch-pad paper and the bond paper used for Government correspondence. Another measured volume of alcohol was then added and the mixture tested as before. The addition of alcohol was continued until the lines were strongly feathered. With 10 volumes of the standard blue-black writing ink and 3.5 volumes of alcohol, there was slight feathering on the inferior paper, as there was on the bond paper when the alcohol was increased to 4 volumes. With the standard red writing ink, feathering was produced on the pad paper by 3 volumes of alcohol and on the bond paper by 4 volumes.

Acetone is considerably more volatile than alcohol, so its effect upon red ink was tried. With scratch-pad paper there was more feathering than with alcohol, but on the bond paper there was none when 11 volumes of acetone was mixed with 10 of the ink.

In every case, beginning with the unmixed inks, the medium and heavy lines showed a spreading of the ink beyond the limits of the two parallel scratches made by the pen. Also, when the lines were feathered, some penetration of the ink to the reverse side of the paper occurred. As the proportion of alcohol or acetone to ink was increased, there was a distinct tendency for the lines to become broader. However, a line was not considered as being feathered unless its edges were noticeably uneven.

3. PRUSSIAN BLUE INKS

Prussian blue is not a dye, but it has as great coloring power as some dyes. It is ordinarily quite insoluble in water, but a kind known as soluble prussian blue can be prepared. It does not form a true solution, as salt, sugar, and many other substances do. It is more like the suspensions of carbon and clay that have been mentioned, but the particles of blue are so small that the suspension, or "colloidal solution", looks perfectly clear. The blue is first formed as an insoluble precipitate, which must be washed until all the salts it contains are removed. It is then soluble in water.

The salts can be removed most easily by dialysis, because the precipitated blue soon so clogs an ordinary filter that water will barely pass through a comparatively thin layer of the pasty precipitate. To wash as little as 10 g of prussian blue on a filter may take 3 or 4 weeks, and because it runs through the paper towards the end of the washing much of it may be lost. Prussian blue is formed when ferric salts and a ferrocyanide, both dissolved in water, are mixed. It is said that there should be an excess of ferrocyanide in order to get a good soluble blue. Perhaps the principal reaction is as follows:

$$\underset{270.3}{FeCl_3.6H_2O} + \underset{422.3}{K_4(Fe(CN)_6)} = \underset{306.8}{FeK(Fe(CN)_6)} + 3KCl + 6H_2O.$$

From the molecular weights given below the equation the weights of ferric chloride and of potassium ferrocyanide needed to make a desired weight of prussian blue can be calculated, but only approximately, for there are unavoidable losses, as well as at least two other reactions. Suppose it is desired to make 30 g of the blue, which is about as large a quantity as can be handled readily, there will be needed 27 g of ferric chloride. This is dissolved in 500 ml of water, and the solution is cleared by adding a few drops of hydrochloric acid. The solution should not be brown and slightly cloudy, but of a clear, bright yellow. The weight of potassium ferrocyanide will be 42.2 g, plus an excess of, say, 10 percent, or 46 to 47 g in all. This is dissolved in 500 ml of water in a 1-liter beaker. The iron solution is then poured, a little at a time and with vigorous stirring, into the solution of ferrocyanide. The precipitate is allowed to settle overnight, the layer of clear solution above the precipitate is removed, preferably by suction or siphoning, and the beaker is filled by adding distilled water. After the precipitate has been stirred, it is again left to settle. When the blue has been washed a few times in this way, it will no longer settle well. The contents of the beaker are then poured into a large funnel with a close-fitting filter paper, and the water is allowed to drain off as completely as it will. The pasty mass is now transferred to a bag made by wetting a large square of ordinary, not waterproof, Cellophane, and gathering and tying the edges around the stem of a funnel. Most of the transferring can be done by scraping the pasty mass from the filter and placing it upon the middle of the wet sheet of Cellophane, before it is tied around the stem of the funnel. What adheres to the filter is transferred with the aid of a jet of water from a wash bottle. When this is accomplished, the funnel is removed from the bag, and the latter is hung in a 4-liter beaker nearly filled with distilled water. The water should come not quite up to the level of the mixture in the bag. Although the excess of ferrocyanide and the potassium chloride formed in the reaction pass out into the distilled water, water also passes into the bag and may fill it if it is immersed too deeply in the water. For this reason the bag must be made of a piece of Cellophane at least 20 inches square. The water in the beaker must be renewed at least once a day, for at least a week or 10 days. When it is believed that the salts have been washed out, take a drop of the liquid out of the bag and let it dry in the air. Then put a drop of distilled water on the dried residue. If the prussian blue has been washed enough, it will at once dissolve in the water. Otherwise, the dialysis must be continued for a few more days.

The thoroughly washed prussian blue will run through any filter, so the only way to get the dry substance is to hang the Cellophane bag and its contents in a warm place for the water to evaporate. When the mass dries to a stiff paste, the top of the bag can be cut off and discarded. It is generally discolored with ferrocyanide. Then spread the bag open, so the paste will dry more rapidly. Attempts to hasten the drying by heating, even to the temperature of boiling water, is apt to cause much of the blue to become insoluble.[16]

Solutions made by dissolving 5, 10, and 15 g of prussian blue, prepared in the way just described, in a liter of distilled water, when kept for nearly 4 years deposited not more than traces of sediment. During this time the solutions were kept in the dark, or in dim light, though this probably had no influence on the result. When a 0.5-percent solution, in a corked bottle, was exposed to summer sunlight

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[16] It may be noted in passing that long-continued dialysis failed to make cupric ferrocyanide soluble, and that a suspension of the brown compound in water was not made clear by the addition of oxalic acid.

at a south window for 56 days, there was no precipitation of the prussian blue. Other solutions of the same lot of blue were made with different small amounts of oxalic acid, because this is usually a component of prussian blue writing inks. These solutions kept no better than those made without oxalic acid.

Various published formulas for prussian blue ink require amounts of oxalic acid equal to one-fourth, or even one-half of the weight of the dry blue. The best results are obtained if the mixture of blue and acid is just covered with water and allowed to stand for several hours before adding the full amount of water called for. The peculiar action of oxalic acid upon prussian blue can be taken advantage of for making really soluble blue, without starting with ferric chloride and potassium ferrocyanide. Commercial prussian blue, for instance the finely powdered form sold as a paint pigment, is mixed with one-fourth its weight of oxalic acid and enough water to make a thin paste, and after about 24 hours is transferred to a Cellophane bag and dialyzed. Without oxalic acid the pigment can not be made soluble by dialysis.

Writing done with prussian blue ink is very fast to light and to water. It is not easily removed by the usual two-solution ink eradicator. The ink is commonly sold as "acid-proof", but nothing is said about the ease with which alkaline solutions will destroy the color. Alkalies, even soap and water, decompose the blue and leave behind a rusty stain of iron oxide, which can be dissolved by treatment with a dilute acid.

A solution of 10 to 15 g of prussian blue in 1 liter of water has a satisfactory depth of color. Because bright blue ink is not popular, sometimes a dye is added to darken the shade and to produce what is sometimes called blue-black ink. This name is unfortunately chosen, because it is commonly understood to mean iron gallotannate ink.

This Bureau has spent but little time in experimenting with dyes for darkening prussian blue inks, because they are not used by the Government and are of little commercial importance. Water-soluble nigrosine (C.I. 865; Sch. 700), when added to solutions of prussian blue and oxalic acid, soon formed gummy deposits. Three other black dyes, durol black *B* (C.I. 307; Sch. 265), Columbia fast black *FF* (C.I. 539; Sch. 436), and direct deep black *RW* (C.I. 582; Sch. 463) were tried, but gave poor results. When the mixtures with prussian blue stood in corked glass tubes for a week, there was no visible settling out of the color, yet they had a curdled appearance when used as writing ink, with a pen that was supposed to be gold-plated. It is suggested that those who are sufficiently interested should either try other black dyes, or else hunt for a yellow and a red dye that can be mixed with the solution of prussian blue, without causing jelling or precipitation. If added in the right proportions to the solution of blue, the red and yellow will produce a practically black solution.

4. COLORED DRAWING INKS

In telling about carbon inks it was pointed out that black drawing ink is not a solution, but only a suspension, of carbon in a liquid vehicle. A few of the commercial colored drawing inks are suspensions of pigments in a liquid. These pigments are usually dye "lakes", formed by precipitating a dye on an inert material, such as aluminum hydroxide, barium sulphate, or some other compound. As the lakes are, in general, of greater density than carbon, and are not in such fine particles at the outset, the problem of grinding them so fine that they will not settle to the bottom of the liquid is more serious than with carbon. The few pigment inks that the Bureau has examined had a decided tendency to settle. Most colored drawing inks are clear solutions of dyes. They do not have the same degree of hiding power as the inks which contain the comparatively opaque pigments, but their good working qualities outweigh the disadvantage due to their being transparent.

The first Federal specification for colored waterproof drawing ink gave formulas for making inks of several colors to serve as standards for fastness to light and water. Although these standard inks were given what was thought to be an adequate test in the laboratory, at the Panama Canal Zone, and in a Bureau where a great deal of drafting is done, two or three of them developed serious faults in the course of a year. It became necessary to cancel the specification, pending more laboratory work. The present Federal Specification TT–I–531 is based upon the work described in this section.

Making a really waterproof ink, which when dry will not be blurred by accidental wetting, nor by cleaning with a damp cloth, is something that can not be done offhand. The ink must contain materials that are soluble in water, but become insoluble when they dry on paper or tracing cloth. The usual combination is shellac and borax, together with dyes that have enough affinity for the shellac to make them resist the solvent action of water. By no means all dyes are suitable, because many of them can be leached out of the shellac-borax film.

The development of satisfactory formulas for drawing inks of seven colors required a great deal more work than had been anticipated. It did not suffice to use a more concentrated solution of shellac and borax in the same proportions as at first, but it was found that if the amount of shellac in a liter was increased, the quantity of borax lessened, and ammonia added to give sufficient alkali for dissolving the shellac, inks could be made that were extremely resistant to water. This was true if the dyes were such that they were held in combination with the shellac-borax film. Otherwise there was no improvement. Only an outline of the work can be given here, and the reader is referred to the original article describing what was done.[17]

A solution was made by digesting, on a steam-bath, 65 g of dry orange shellac in 500 ml of a mixture of 1 volume of strong ammonia water (sp gr 0.90) and 4 volumes of distilled water. When the shellac was dissolved, the solution was cooled and extracted four times with a mixture of ethyl ether and petroleum ether, to remove the insoluble waxy component of the shellac. The solution was analyzed to determine its content of shellac, and it was then diluted with enough water to bring the content of shellac down to 50 g in 500 ml. To the still slightly ammoniacal solution 1 g of phenol and 3 g of crystallized borax were added. No attempt was made to bleach the shellac solution, because it was found that the coloring matter in the unbleached solution did not affect the hues of pale dyes enough to be noticeable.

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[17] E. W. Zimmerman, *Colored waterproof drawing inks*. Ind. Eng. Chem. 25, 1033 (1933).

This stock solution was used for making the actual inks, by mixing it with equal volumes of solutions of suitable dyes. Before use, the ink was filtered to remove any insoluble matter from the dye or that was not removed from the shellac. In all, 92 dyes were tried, and the most promising, as regards water-fastness and good color, were made into inks, and 2 bottles of each were stored for testing their keeping quality. The best of the 92 dyes, and the weight of each that was dissolved in 50 ml of water and mixed with an equal volume of the shellac solution, are given in table 1. The dyes marked "second choice" made ink that did not keep quite so well as that made with the "first choice" dyes. Yet all 16 dyes made inks that were in good condition at the end of 2 years, with the exception of 1 of the 2 samples made with crystal violet. In this the color was destroyed by a heavy growth of mold, but the duplicate sample was in good condition.

TABLE—*Dyes for drawing inks*

FIRST CHOICE

Name of dye	Colour Index number	Schultz number	Gram
Erythrosin, yellowish	772	591	0.5
Brilliant orange *R*	78	79	.6
Chloramine yellow	814	617	.4
Brilliant milling green *B*	667	503	1.2
Wool blue *G* extra	736	565	.5
Methyl violet *B*	680	515	.5
Benzamine brown *3GO*	596	476	.8

SECOND CHOICE

Name of dye	Colour Index number	Schultz number	Gram
Crocein scarlet *3B*	252	227	0.5
Benzopurpurine *10B*	495	405	.6
Orange R	161	151	.4
Metanil yellow	138	134	.8
Thiazol yellow	813	198	.8
Malachite green	657	495	.8
New methylene blue *N*	927	663	.4
Crystal violet	681	516	.4
Benzo brown *G*	606	485	.6

5. SHOW-CARD INKS

The Bureau never has occasion to test show-card inks but is now and then asked how to make them. A few of the formulas to be found in books are given here.

Many of the formulas are based upon a solution of shellac and borax similar to that described in the preceding section. The solution could be made in the same way as for colored drawing inks, but the extraction with the mixture of ethers could be omitted and the solution simply filtered or perhaps strained through muslin or other closely woven material. Before being filtered, the solution is clouded with extremely fine particles of the insoluble waxy component of the shellac. This tends to clog the pores of the filtering medium, so that after a time the liquid runs through very slowly. There will be less trouble from this cause if the solution is allowed to cool first, because the wax is sticky when hot. To make ink with this solution, dyes of the desired colors are dissolved in it but in larger amounts than suffice for drawing inks. Because the requirements for a showcard ink are less exacting than for a drawing ink, other dyes than those named in the preceding section can be used.

Instead of dissolving dyes in the shellac-borax solution, dye lakes or other pigments could be suspended in it. First, the pigments would have to be ground very thoroughly with enough of the solution to make a thin paste, and this would then be thinned to a good working consistency by adding more of the solution. Inks made in this way would have better hiding power than the clear solutions of dyes, but it is an open question whether this advantage would pay for the extra trouble, unless the grinding is done with an ink mill. Grinding by hand is slow and inefficient, and unless it is done thoroughly the resulting ink will not be smooth but lumpy.

A formula that is typical of those found for black ink is: Dissolve 16 parts by weight of asphaltum and 18 parts of venice turpentine in 50 to 60 parts of turpentine, and add 4 parts of lampblack.

6. HECTOGRAPH INKS

The hectograph is a simple device for making a moderate number of facsimile copies of a letter or drawing. The original is pressed down upon a special surface or pad composed of gelatin (or glue) and glycerin, or of clay and glycerin. The pad absorbs part of the ink of the original and can then be used for printing upon other sheets of paper. "Hectograph" means " hundred writing", but this name seems exaggerative.

Hectograph ink must contain a large proportion of a dye that has good color strength. With the idea, afterwards abandoned, of writing a Federal specification for this ink, numerous samples were made and tested, in order to find out which dyes would give the largest number of good copies. The inks were made by a formula obtained from the U. S. Government Printing Office, except that in it acetone was substituted for alcohol. The formula, in parts by weight, is:

Acetone	8
Glycerin	20
Acetic acid, 28-percent, commercial	10
Water	50
Dextrin	2
Dye	10

If the unit of weight is 1 g, this will make a little more than 90 ml, or about 3 fluid ounces of ink.

The dextrin is first dissolved in the water, which must be heated, but need not be boiled. Care must be taken not to char the dextrin at the start, when it clings to the bottom of the vessel in a sticky mass. It is safest to heat the mixture by setting the container in a vessel of hot water. When a clear, or nearly clear, solution is obtained, cool it and add the other liquids. Acetone is combustible, and quite volatile, but the amount in the ink is not dangerous. If it should be poured into the hot solution, there would be a brisk boiling, and much of the acetone would be lost.

In the tests referred to, the following dyes were selected as giving the greatest number of copies of satisfactory intensity. The best of all is methyl violet *B* (C.I. 680; Sch. 515). Crystal violet (C.I. 681; Sch. 516) is nearly as good. For red ink, rhodamine *B* (C.I. 749; Sch. 573) was selected, with fuchsine, or magenta (C.I. 677; Sch. 512), as second choice. Fuchsine is so slightly soluble that only 3.5 parts of it, instead of 10, could be dissolved in 90 parts of the solvent.

For green and blue, emerald green (C.I. 662; Sch. 499) and victoria blue *B* (C.I. 729; Sch. 559) ranked first, with malachite green (C.I. 657; Sch. 495), and soluble blue (C.I. 707; Sch. 539), second.

With a clay-glycerin pad and inks made with these dyes, it was possible to get at least 30 copies in which the strokes of the pen were unbroken, and numerous other copies that were easily legible, though with more or less broken lines. With some of the numerous dyes tested, this could not be done.

There is no truly black water-soluble dye, for dilute solutions of all the so-called black dyes are blue or purplish. Hectograph ink made with water-soluble nigrosine (C.I. 865; Sch. 700) will make one or two nearly black copies, but the succeeding ones are of a dingy purplish gray. It is possible to make black ink by mixing dyes, for instance green, violet, and yellow, in the right proportions, but because the dyes will not be absorbed by the hectograph pad nor by the sheet of paper in the same proportions, no black copies can be made after the first one or two.

A bright yellow ink made with auramine (C.I. 655; Sch. 493) was almost illegible, on account of a curious optical effect. Its brightness was nearly the same as that of the white paper. Because of that and of its light color, there was no great contrast between it and the paper, and the copies looked so extremely blurred as to be illegible. When seen through a blue glass, which made the ink look dark, the copies were sharp and distinct.

There are simpler formulas for hectograph inks in various books, but they have not been tested by the Bureau. Because a single name may be given to two different dyes, the Colour Index and the Schultz numbers are omitted from the formulas given here. It is probable, though, that the methyl violet and the fuchsine are the same as those in the fourth preceding paragraph, and that Hofmann's violet is C.I. 679; Sch. 514. In these formulas all parts are by weight.

Blue.—Aniline blue, water-soluble, 1; glycerin, 1; water, 5 to 10.

Indigo-blue.—Brilliant green, 3; Hofmann's violet 4*B*, 3; glycerin, 1; water, 10.

Green.—Aniline green, water-soluble, 3; glycerin, 2; water, 10; alcohol, 2.

Red.—Fuchsine, 1; glycerin, 1; water, 5; alcohol, 1.

Violet.—Methyl violet, 1; glycerin, 2; water, 7.

7. STAMP-PAD INKS

Federal Specification TT–I–556, for stamp-pad ink, gives a formula for a standard in several colors. The vehicle, or liquid part, consists of 55 parts by weight of glycerin and 45 parts of water. Equal volumes of U.S.P. glycerin (sp gr 1.249; 96-percent), and water will make almost exactly the desired mixture.

Five parts of dye is dissolved in 100 parts of the solvent. The dyes required by the specification are fuchsine (magenta; C.I. 677; Sch. 512), light green *SF* (C.I. 670; Sch. 505), soluble blue (C.I. 707; Sch. 539), acid violet (C.I. 698; Sch. 530), and water-soluble nigrosine (C.I. 865; Sch. 700). A great variety of other dyes can be used, if desired.

At ordinary temperatures glycerin practically does not evaporate, and it is hygroscopic, or attracts moisture from humid air. This keeps the ink from drying on the pad, even in winter, when the air in heated office buildings is of desert aridity. In summer, when the air is usually of high humidity, the ink tends to take up water from the atmosphere. There is not enough change in the ink, with variations of atmospheric humidity, to affect its use.

8. RECORDING INKS

There are numerous kinds of instruments for making continuous records of temperature, barometric and steam pressures, electric voltage, etc. The record consists of a line or of a series of dots on a circular card or a long roll of paper. The instrument may have to run a long time without attention, so there must be an ample supply of ink of a kind that will not dry on the pen, if the instrument is located indoors, nor freeze at outdoor temperatures in winter. For many years the United States Weather Bureau has used recording ink made like stamp-pad ink, but with much less dye. The mixture of equal volumes of glycerin and water is a good "antifreeze", yet there are parts of the country where it would be solid in winter. To overcome this difficulty, enough alcohol to keep the ink fluid at any winter temperature is mixed with the ink. For indoor use, a mixture of 1 volume of glycerin and 3 volumes of water has been found to make satisfactory recording ink.

The properties of glycerin that make it so valuable in stamp-pad and recording inks are disadvantages as soon as the ink is put upon paper. Because the ink must dry almost entirely by being absorbed, the marks are apt to be "feathered", or have uneven edges. The ink spreads in all directions from the actual marks made by the pen, and does not just go down into the paper. Whether or not the ink feathers depends upon the paper or card on which the record is made, and also upon the nature of the dye in the ink. In order to get definite information on this subject, a number of experiments were made with inks prepared by dissolving selected dyes in glycerin and water in the proportions used for both outdoor and indoor recording inks. Inks were also made with similar mixtures of ethylene glycol and water, because the glycol is in many respects similar to glycerin, though somewhat more fluid.[18]

In the first series of tests, 12 acid and 7 basic dyes were made into 38 inks, by dissolving them in each of the 2 mixtures of glycerin and water already mentioned. Lines were drawn on five kinds of paper, including three heavy papers, or thin cards, furnished with recording instruments. The lines were drawn with an ordinary pen, and were inspected after they had dried naturally. According to their appearance the lines were rated as *N* (no feathering), *SF* (slight feathering), and *F* (decided feathering). The results showed that neither the acid nor the basic dyes could be considered as superior. Of the total 190 lines drawn on the 5 papers with the 38 inks, 10 were rated as *N*, 108 as *SF*, and 72 as *F*. It must be admitted that most of the lines rated as *SF* would be considered as quite satisfactory for most uses.

It was thought that direct dyes might make better inks than the acid and basic dyes. Direct dyes, as their name implies, are taken up directly by vegetable fibers, without the aid of mordants to fix them on the fibers by forming insoluble compounds. It was thought that direct dyes would not spread in the paper when the mixture of glycerin and water was absorbed, and that therefore the lines made with the inks would have smooth edges.

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[18] C. E. Waters, *Inks for recording instruments.* J. Research NBS 17, 651–655 (1936) RP935.

In all, 16 direct dyes were made into 64 inks, by dissolving them in the 2 mixtures of glycerin and water, and in equally diluted ethylene glycol and water. The table of results leads to three general conclusions: Inks made with direct dyes feather much less than those made with acid and basic dyes; glycerin at either dilution is a better solvent than equally diluted ethylene glycol; and, as might have been predicted, the greater the proportion of water in the ink, the less is the tendency to feather.

Feathering Tests of Inks Made With Direct Dyes

Rating	Glycerin-water		Glycol-water	
	1:1	1:3	1:1	1:3
Total *N*	52	79	27	69
Total *SF*	21	1	15	11
Total *F*	7	0	38	0

It is not necessary to tell the names of the acid and basic dyes that were used in the tests, but the list of direct dyes may be of interest to some readers. There are 17 dyes in the list, but the yellow one was not rated, and does not show in the summary of the results of the tests given in table 2. Its pale color and brightness made so little contrast with the paper that it was impossible to decide how to rate the lines drawn with it. However, it might be used to mix with other dyes, for instance with blue, to make bright green.

One of the dyes, toluylene orange *R*, did not make a clear solution, so it might eventually cause trouble if used for a long time, by gradually clogging the pen. Another of the dyes, diamine green *B*, set to a sort of soft jelly on standing overnight, but this became quite fluid when shaken, and there was no trouble about drawing the lines with it. The two green dyes made inks of a rather dull color.

Table 2.—*Direct Dyes for Recording Inks*

Name of dye	Colour Index number	Schultz number
Benzo fast scarlet	326	279
Congo red	370	307
Toluylene orange *R*	446	362
Toluylene orange *G*	478	392
Pyrazol orange	653	---------
Chloramine yellow	814	617
Chloramine green *B*	589	470
Diamine green *B*	593	474
Diamine sky blue *FF*	518	424
Benzo sky blue	520	426
Diamine violet *N*	394	327
Oxamine blue *4R* (Erie violet *2B*)	471	385
Bismarck brown *R*	332	284
Benzamine brown *3GO*	596	476
Columbia black *FF* extra	539	436
Direct deep black *RW* (Erie black *RXOO*)	582	463
Direct deep black *RW*[a] (Erie black *RW*)	582	463

[a] There were 2 samples of this dye, from the same manufacturer but with different names on the labels. One gave a deeper color than the other, when dissolved in the same concentration.

When the inks made with direct dyes had been kept in corked glass tubes for 12 weeks, some of the corks were moldy. Of the inks made with the mixture of equal volumes of glycerin and water, six had moldy corks. With the more dilute glycerin, 13 of the corks and 3 of the inks themselves were moldy. No mold was seen on any of the corks that had been wet with the inks made with ethylene glycol, at either dilution. It might be concluded that the glycol is a better preservative than glycerin, but this would have to be confirmed by further experiments.

9. INDELIBLE MARKING INK FOR FABRICS

Federal Specification TT–I–542 for indelible marking ink for fabrics, gives no formula for a standard ink. Of the numerous formulas to be found in books, nearly all are for inks made with silver, or are of the aniline black type.

Although silver ink looks black in the bottle, and makes moderately dark marks on fabrics, its full color must be developed by heat or by exposure to bright light. Either treatment causes the reduction of the silver salt in the ink, so that metallic silver is deposited in and on the fibers. The metal is so finely divided that it looks black. An old formula, slightly modified, is given in the next paragraph.

Dissolve 5 parts of silver nitrate in its own weight of water, and then add ammonia water in small amounts until the precipitate that first forms is dissolved In separate vessels dissolve 3 parts of anhydrous sodium carbonate in 15 parts of water, and 5 parts of gum arabic in 10 parts of warm water. Pour the three solutions together and warm gently until the mixture starts to darken. If 1 part equals 1 g, the formula will make about 35 ml, or a little more than a fluid ounce of ink. This formula has been used for several years by an institution, in the District of Columbia, where the laundering conditions are severe, and where other inks that were tried soon washed out.

"Household" ammonia is generally not suitable, because it is apt to contain other substances than ammonia gas and water. Pure ammonia water can be obtained from a druggist, and he should be able to supply sodium carbonate monohydrate, if not the anhydrous form. The monohydrate contains 14.5 percent of water of crystallization, so 3.5 parts of it must be used, as the equivalent in alkali of 3.0 parts of the anhydrous salt. The small additional quantity of water, 0.5 part, thereby added will make no practical difference.

Metal vessels should not be used for preparing the solution of silver nitrate, nor for the finished ink. It is simplest to dissolve the silver nitrate in the bottle in which the ink is to be kept. The salt is easily soluble, and the water does not need to be heated. The other two solutions can be poured into the bottle, and if they are warm enough, no further heating may be required to darken the mixture. This final step in the preparation of the ink is not necessary, but is convenient because it is easier to use a dark ink than a pale one. If the freshly mixed ink does not darken, set the bottle cautiously in a vessel of warm water.

Because of the chemical action of steel upon silver ink, a gold pen, or if it can be had a quill pen, should be used with the ink. Lacking these, use a new steel pen, or a gold-plated one. When the marks are dry, press them with a hot flatiron, or place them in full sunlight, to develop the black color. The marks will then be very resistant to washing, unless the laundry uses too strong a solution of chlorine as the "bleach", in which case the silver will soon be converted into silver chloride. This is not very soluble in water, yet sufficiently so to be washed out of the fabric in a short time.

There are formulas for silver marking inks colored with dyes, but they seem to have no advantage over black ink. In fact, the silver in the ink soon makes the marks turn black, and the dye washes out.

Aniline black is extremely fast to light and to washing, so it is suitable for marking ink. Possibly the water-insoluble forms of some of the black dyes are also used in commercial indelible inks. The Bureau has never made inks of either kind, and rarely has occasion to test samples. The formula about to be given is typical of those for the development of aniline black. The ink consists of two solutions which are to be mixed immediately before use. In the formula, all parts are by weight.

Solution A

Copper (cupric) chloride	85
Sodium chlorate	106
Ammonium chloride	53
Water	600

Solution B

Gum arabic	67
Aniline hydrochloride	200
Water	335

For use, mix 1 volume of *A* and 4 volumes of *B*. The marks need not be exposed to sunlight nor ironed to develop their color.

Sodium chlorate is quite different from sodium chloride, common salt. The chlorate is extremely dangerous when mixed with combustible substances, because friction or shock may cause the mixture to explode with great violence. Potassium chlorate is easier to obtain than the sodium salt, but it can not be used in this formula, because it is not sufficiently soluble in water. To dissolve 122 parts, which is chemically equivalent to 106 parts of sodium chlorate, would require about 1,900 parts of water at ordinary temperatures.

An aniline black ink to be used with a rubber stamp is made as follows: Grind separately, and as fine as possible, 20 parts of copper sulphate crystals (bluestone) and 30 parts of aniline hydrochloride (aniline salt). Mix the two, add 10 parts of dextrin, 5 parts of glycerin, and then water in small portions until the mass has the right consistency.

An interesting development of recent years is an invisible laundry ink. Marks made with it can not be seen unless illuminated by a special lamp that gives a great deal of ultraviolet radiation. The marks then glow with a phosphorescent light that is in good contrast with the background of unmarked fabric. The Bureau has not analyzed the ink, and can give no information about its composition.

10. SYMPATHETIC OR INVISIBLE INKS

Persons who indulge in secret writing for legitimate or nefarious reasons must have invisible or sympathetic ink. In their chapter on this subject, Mitchell and Hepworth[19] say that both Ovid (43 B.C.

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[19] Inks, Their Composition and Manufacture, 3d ed. p. 286 (Chas. Griffin & Co., (Ltd.), London, 1924).

to A.D. 17) and Pliny (no doubt the Elder, A.D. 23 to 79) tell about sympathetic inks. They knew of the use of milk and plant juices for this purpose. When heated moderately the writing turns brown before the paper begins to scorch, and thus the message becomes readable. These are but two examples of secret inks that are made visible by heating. Some of the inks char more easily than the paper, but others cause the paper to char. In either case the writing turns brown, or even jet-black.

Without going outside of the home, anybody can get several materials for making sympathetic ink that can be developed by heat. Any of the following substances can be used, though it must be confessed that some of them are very poor indeed: Alum, soda (either baking or washing), borax, flour or starch boiled with plenty of water, a solution of soap or of washing powder, diluted mucilage, milk, lemon juice.

Ammonium chloride, "sal ammoniac", dissolved in 15 to 20 times its weight of water makes an ink that is invisible, but becomes dark brown or black when pressed with a hot iron, or held at a distance above a small flame. This is as good a sympathetic ink as any, is easy to prepare, and is not dangerously poisonous.

The salts of several metals have long been favorite materials for sympathetic ink. These salts are not all colorless when in the solid form, or in strong solution, but invisible marks made on paper with very dilute solutions can be developed by suitable means. Among these salts are lead acetate, ferric sulphate, mercuric chloride (corrosive sublimate, dangerous to handle and very poisonous), copper sulphate, cobalt chloride, and nickel chloride. In addition to being turned brown or black by the fumes of ammonium sulphide, writing with any of the salts can be developed by heat, and still other means can be employed with some of them. For instance, if the ink is made with ferric sulphate, a solution of gallic or tannic acid will turn the writing black, and potassium ferrocyanide will form prussian blue.

Of the salts just mentioned, cobalt chloride is in some respects the most interesting. When a solution of the salt in water evaporates to dryness, the chloride appears in crystals that are red, though not intensely so. If the solution used as sympathetic ink is so dilute as to be only of a moderately deep pink, the thin layer of the salt that is left on paper when the writing dries will not be perceptible. If the writing is kept for some time in rather dry air, or is warmed slightly, the cobalt chloride loses most of its "water of crystallization", and is then so intensely blue that the writing is visible. Exposure to moist air, as by breathing upon it, makes the writing vanish because the blue salt regains water of crystallization and turns red. These changes back and forth can be repeated many times, but if once the secret writing should be heated too strongly when warming it, the chloride will char the paper, and the writing will then be permanently black.

As a means of developing writing done with a variety of inks, iodine is interesting. It is preferably used as the vapor given off by the solid element at ordinary temperatures, though the tincture diluted with water can be employed. If a thin solution of boiled starch was used for the writing, iodine will turn it blue. The color disappears after a time, and more quickly by gentle warming. Writing with a solution of soap becomes yellow or brown because the soap absorbs iodine vapor more easily than paper does. This color soon vanishes because the iodine is so volatile. Copper sulphate and lead acetate are colored temporarily, while marks made with mercuric chloride show as white on a background of yellow paper. If the writing was done with distilled water, iodine vapor will color the letters a little more strongly than the background. The water disturbs the sizing at the surface of the paper, and thus allows the iodine vapor to be absorbed more readily there than elsewhere.

In the examination of a document suspected of containing secret writing, the first step would be to try the effect of ultraviolet radiation, which causes many substances to glow with a phosphorescent light that can be photographed. If this test shows nothing, the next step would be to warm the paper moderately, and small portions of it possibly more strongly. This may not bring out anything, but any latent writing is not apt to be destroyed by the treatment. Exposure to iodine vapor or to the fumes of ammonium sulphide might be next in order, or the fumes of ammonia water could be used. If heat and the various vapors fail, chemical solutions must be tried on selected small parts of the document. To treat the whole sheet of paper with a reagent that brought no visible result might destroy all chance of developing the writing. If a chemical solution applied to a small part of the document shows that there is secret writing, the entire sheet of paper can be treated with the solution. It is safest to do this in a letterpress with cloths moistened with the chemical solution. In this way a minimum of water will be used. If the secret message was written with an easily soluble substance, dipping the sheet into, or brushing it over with, the solution might dissolve the invisible substance and thus destroy the secret writing. In a letterpress, unless the cloths are too moist, there is little flow of liquid, and the danger of hopelessly blurring the writing is reduced to a minimum.

11. INKS FOR SPECIAL SURFACES

All the inks so far taken up in this circular have been intended for use on paper and similar materials, and they are not well adapted to writing on impervious or oily surfaces, such as glass, porcelain, celluloid, metals, or painted surfaces. It is true that by going over the lines repeatedly it is possible to write after a fashion on some of these materials with writing or drawing inks, but the behavior of the ink shows that it is not suitable for the surface. In this section a few formulas are given for inks that will work more or less well on some special surfaces. Many more formulas can be found in books.

(a) INKS FOR CELLULOID

Trial of two published formulas for inks to be used on celluloid showed that they would make permanent marks, because they contained acetone, a solvent for celluloid, so they readily "took" on it. The trouble with the inks was that they spread excessively over the surface, so that with a fine-pointed pen the narrowest line that could be drawn was about one-eighth of an inch wide.

Some years ago it was found that a commercial solution of bitumen in coal-tar naphtha could be used for writing on celluloid. It was necessary to dip the pen into the solution, and then to touch it to the celluloid without an instant's delay, or the point of the pen would become too dry to let the ink flow. The slightly raised letters were quite resistant to rubbing, though they could be erased by means of absorbent cotton moistened with benzol.

The success with this solution led to experimenting with solutions of asphalt in different solvents, and it was found that amyl acetate ("banana oil") gave the best results. A solution concentrated enough to make black marks would not write. A less concentrated solution made rather sharp lines of a dark-brown color.

(b) INKS FOR GLASS AND PORCELAIN

Some of the inks recommended for writing on glass contain sodium silicate solution, or water glass, mixed with pigments that are not changed in color by the alkali in the silicate. Water glass should not be used if the marks are to be removed later because, when the solution dries completely, the silicate forms such a strong bond with the glass that it can not be removed completely without grinding. A typical formula for ink of this kind is to mix 11 parts of drawing ink and 1 or 2 parts of water glass.

Dissolve 4 parts of rosin in 30 parts of denatured alcohol. Separately dissolve 4 parts of borax in 50 parts of warm water. Mix the two solutions and let stand overnight in a loosely corked bottle. Next morning pour off the clear brown solution, and use it for dissolving dyes to make inks of the colors desired. The crystalline deposit on the bottom and walls of the bottle consists chiefly of borax, mixed with a little rosin. Because this ink has a slight tendency to spread on glass, it should be used with a fine-pointed pen.

A similar ink can be made by dissolving dyes in a solution of shellac and borax in water, without alcohol. The solvent is made by heating nearly to boiling a mixture of 4 parts by weight of dry orange shellac, 1 part of borax, and 150 parts of water. It may take 2 or 3 hours to dissolve the shellac. The solution must be filtered, preferably after it has cooled, to remove the insoluble waxy portion, the orpiment that settles to the bottom, and the miscellaneous impurities that shellac always seems to contain. The purplish color of the solution will not interfere noticeably with the hues of the dyes that are dissolved in it to make the ink. From 0.5 to 1 g of dye will usually suffice to make 100 ml of ink. The following dyes are suggested in addition to those named in connection with waterproof drawing ink:

Dye	Colour Index number	Schultz number
Naphthol yellow	10	7
Tartrazine (orange in this ink)	640	23
Diamine sky blue *FF*	518	424
Naphthol blue-black *S* (green-blue)	246	217
Benzo cyanine *R* (verging on violet)	405	336
Durol black *B* (blue-black)	307	265
Nigrosine (purplish or bluish black)	865	700

It should not be thought that this ink cannot be washed from glass. To get such a degree of fastness, water-glass ink or actual etching must be resorted to.

(c) ETCHING INKS FOR GLASS

The Bureau's Letter Circular LC150, Dry Etching of Glass, gives a few formulas, and tells in detail how certified burettes and other glass measuring apparatus are marked. On application to the Bureau, a copy of the Letter Circular will be sent without charge.

(d) INK FOR ZINC GARDEN LABELS

Ink for labels made of sheet zinc is of interest to many gardeners. Perhaps the most durable marks are those made with a solution containing copper, which is precipitated upon the zinc. As the zinc slowly weathers away, the copper in the marks keeps up an electrolytic action, so that the writing persists as very slightly sunken lines of black on the zinc. Labels written with this sort of ink have not been obliterated by exposure to the weather continuously for 5 or 6 years in the climate of Washington. If the writing becomes obscured by the products of the corrosion of the zinc, all that is necessary to restore its legibility is to rub it with the finger to remove the whitish coating.

It is interesting that unless there is a normal amount of rain to wash off the corrosion products, the labels are not very satisfactory, as in a greenhouse where the plants are sprayed at intervals, but where there is not enough spraying to be the equivalent of periodical rains. It helps a little to dip the unwritten labels for a few minutes in a 5- or 10-percent solution of potassium bichromate. This treatment retards the rate of corrosion where the water rests in drops on the zinc, and the writing is less apt to be obscured.

A simple formula for the ink is to dissolve 1 part each of crystallized copper sulphate ("bluestone") and potassium chlorate in 36 parts of water. In the discussion of indelible marking inks there is a caution about handling chlorates, which should be read again.

The ink reacts with zinc so that copper is thrown out of solution in metallic form. A similar reaction takes place with iron, so a steel pen is not the best for writing with this ink. A gold pen should be used, if possible, or a gold-plated one. If these were the days when "penknife" meant what it says, a quill pen would also be suggested. Whatever the kind, it should have a fine point, because the ink has a tendency to spread a little on the surface of the zinc. If the metal is reasonably clean, it is best to write on it directly, but sometimes it must be cleaned with sandpaper. After this it should be rubbed with the fingers, for without the slight film of grease thus applied, the ink may spread and make only unreadable blurs.

(e) INK FOR BRASS

Instruments makers sometimes give brass a fine mat black finish by dipping the perfectly clean metal into a solution made by dissolving copper carbonate in ammonia water. This suggested trying ink made by dissolving the more easily obtainable copper acetate in 15 times its weight of water, and adding to this enough strong ammonia water to dissolve the blue precipitate that is first formed. This makes good black marks on brass, but not on copper, because the blackening is caused by a chemical reaction between the copper in the solution and the zinc in the brass. A similar solution of copper sulphate does not make as black marks as the acetate solution.

(f) INK FOR OTHER METALS

Inks made by the first two formulas for writing on glass and porcelain are said to be good for use on metals also.

A dilute solution of silver nitrate in water makes black marks on tin, brass, copper, and other metals. The marks will be still better if ammonia water is added to the solution of silver nitrate. At first a black precipitate is formed, but more ammonia will dissolve it. This solution makes beautifully sharp, black lines. It has the disadvantage that the silver compound formed by the action of the ammonia is explosive. It seems to be safe so long as it is in solution, but the solid left behind when the water evaporates is sensitive to shock, and may explode with great violence if handled roughly. The crusts that sometimes form around the cork of the bottle in which the solution is kept are the explosive compound. If any such deposit is noticed, it should be rinsed off. To try to wipe it off may cause it to explode.

For writing on aluminum, the solution of shellac, borax, and dye that was recommended for glass is quite satisfactory.

(g) TIME-CARD INK

On letter boxes in the smaller towns, the hours at which mail is collected are written on white lacquered cards. The specification under which the ink is bought requires that it shall be at least as permanent as ink made as follows: Mix 25 parts of shellac varnish (4 pounds to the gallon), 10 parts of denatured alcohol, and 15 parts of technical cresol. In this dissolve 5 parts of nigrosine base (C.I. 864; Sch. 698). This ink can be used for writing on a variety of surfaces, and would no doubt be found useful for garden labels not made of zinc.

IV. THE TESTING OF INKS

An essential part of each Federal specification for an ink is the section in which the methods of testing are described. If the specification gives a formula for a standard ink, both the sample and the standard are subjected to the same tests, and so far as possible on the same sheet of paper. The chief reason for having a standard ink is to use it as a basis for comparison in the testing, because any dissimilarity between it and the sample becomes apparent at once. If the sample is a red ink, or a stamp-pad ink, it need not match the standard in color, unless this has been agreed upon by buyer and seller. However, the sample must be as satisfactory in working qualities as the standard, and as fast to light.

1. IRON GALLOTANNATE INK

Both kinds of iron gallotannate ink can be considered together, because exactly the same test methods are employed for both. The tests follow naturally from the definition of ink given by Schluttig and Neumann, which is quoted on an earlier page of this circular. The definition clearly tells what properties the ink should have, and the tests are designed to find out whether the sample has these properties. In the fifth chapter of their book, their testing procedure is given, together with detailed explanations of the tests, some of which are not required by the Federal specifications. Schluttig and Neumann do not give a corrosion test.

Because freshly made, well-settled ink should be clear, the first step in the examination of a sample is to allow the ink to remain undisturbed for 24 hours. If the sample is in several small bottles, which together contain the pint of ink called for, the contents of the bottles are poured into a single one of a suitable size. If the sample is concentrated ink, it is diluted with the requisite volume of water and thoroughly mixed. Powders and tablets are dissolved in water. In any case, after 24 hours, the bottle, which has not been disturbed meanwhile, is held up against the light, and is slowly tilted to see whether any sediment is at the bottom. There should be at most only traces of sediment. Very muddy ink can be rejected without making any tests.

If the ink passes this inspection, the test for keeping-quality is started next, because it takes 2 weeks to complete. In two similar clear glass vessels, for instance, crystallizing dishes 50 mm (2 inches) in inside diameter and about 45 mm (1¾ inches) deep, are placed 25-ml portions of the sample and of the standard. The dishes, loosely covered, are kept where they will be in diffused daylight, but never in direct sunlight, for 2 weeks. At the end of this time, the sample should show no more surface skin than the standard, nor more deposit on the bottom and walls of the container.

The iron content of the sample is determined in a 10-ml portion, by any suitable analytical procedure. The amount of iron in 100 ml of copying and record ink should not be less than 0.58 g, nor more than 0.70 g. For writing ink the limits are 0.29 and 0.35 g.

Streaks are made side by side on white bond paper with the sample and the standard. The sheet of paper, 8 by 10½ inches, or of any other convenient size, is pinned to a board or clamped to a pane of glass, and held at an inclination of about 45°. When arranging the sheet of paper, it is desirable to place it so that the ink streaks will be made in the "machine direction", or lengthwise of the long band in which it comes from the papermaking machine. Although the fibers of paper seem to be arranged haphazardly, there is a definite difference in some of the properties of the sheet in two directions, one the machine direction and the other at right angles. If a piece of paper about an inch square is laid upon water, in a moment or two it starts to curl up on opposite sides, thus making a shallow trough. The axis of this trough is parallel to the long direction of the paper as it comes from the papermaking machine. This should be the direction in which the ink is made to flow when making streaks. If the ink flows across the machine direction, the paper will become wrinkled across the streaks, which will then be unevenly colored.

Measured portions, of about 0.6 ml each, of ink are allowed to flow down across the sheet of paper. The ink is measured in a pipette made of glass tubing of 3.5 mm (⅛ inch) bore, and 250 mm (10 inches) long. A mark is etched or scratched 60 mm (2⅜ inches) from one end of the tube. These are only approximate measurements, because the exact volume of ink is of no great importance. The ends of the tube can be fire-polished, but they should not be constricted. Ink is drawn up to the mark, and kept from flowing out by pressing the tip of a finger against the upper end of the tube. While holding the tube vertically, its lower end is held against the upper edge of the inclined sheet of paper, the finger removed, and the ink is let flow out all at once and down across the paper. One or two more streaks are made with the sample ink and then, with another pipette, streaks of the standard, close beside those of the sample. The sheet of paper is left in position until the streaks are dry, and is then put where it will be in diffused daylight, not in direct sunlight.

It is not necessary, according to the specification, that the freshly made streaks of the sample and of the standard shall be of exactly the same color, though they should be equally uniform in color. They should be of about the same shape and width, because these features indicate that the two inks are about equally fluid—an exact measurement would be a waste of time. The streaks made with the sample should show no more evidence of striking through the paper than do those of the standard.

After being kept in diffused daylight for a week, the streaks of the sample should be as intensely black (in reality blue-black) as those of the standard. The bottom half inch of the sheet is cut off and discarded. Then five strips, each about an inch wide, are cut from the lower end of the sheet. One strip is soaked in distilled water for 24 hours, the next strip is kept away from intense light and laboratory fumes. The third strip is soaked in a mixture of equal volumes of denatured alcohol and water for 24 hours. The fourth strip is also put away for later comparison, and the fifth is exposed at a distance of about 10 inches from a glass-enclosed carbon arc for 48 hours. When an arc lamp is not available, the test can be made by exposing the writing to direct sunlight, on the outside sill of a window facing south, but about double the number of hours will be required. In these three tests the sample should retain its color as well as does the standard. The comparison is made easier with the aid of the two strips, the second and fourth, that were set aside.

Because of the temptation for the manufacturer to increase the amount of free mineral acid in his ink, so as to delay the deposition of sediment, a test of the corrosive action of the ink upon steel pens is made. This test is of no interest to the millions of users of fountain pens, because gold is not attacked by the acids that are in ink. The millions of users of steel pens must be looked out for. It is incredible how many steel pens are sold each year. In the fiscal year beginning July 1, 1932, the Post Office Department alone asked for bids on 5,212,800 steel pens.

The amount of metal dissolved from the pens is a rough measure of the acidity of the ink, and its determination may have some value in preventing the use of excessively acid ink for writing that must be kept for a long time.

To make the corrosion test, take two new steel pens, from the same box, for each of the samples, and two for the standard ink. Rinse the pens with alcohol, then with ether, and dry them in an air-oven at 105° C (221° F). Weigh each pair together to the nearest milligram. Because the preliminary washing is to remove the oily film from the metal, the pens should afterwards be handled with forceps. Immerse each pair of pens in 25 ml of ink, contained in a small beaker or flask, taking care not to have them "nested" together. After 48 hours, remove the pens, clean them with water and by rubbing to remove the tightly clinging deposit, rinse them with alcohol, and dry at 105° C. Again weigh, and if the loss in weight of the pair of pens in the sample is greater than the loss in the standard ink, the tests should be repeated with both inks and with new pens, to check the first results.

Ink that contains oxalic acid usually forms on the pens a yellow crust of ferrous oxalate, which is not easy to remove by washing and scrubbing. To get rid of the crust, wash the pens with water and then, with forceps, hold them one at a time a few inches above a small flame, but do not heat them to redness. As soon as the crust blackens and ceases to smoke, drop the hot pens into water. It will then be comparatively easy to clean them in the regular way.

The weight of metal dissolved depends to some degree on the surface area of the pens. This would not be true if corrosion stopped as soon as all the free hydrochloric or sulphuric acid was neutralized by dissolved iron. Rupert [20] showed that when pens are immersed in dilute solutions of hydrochloric and other acids, "an amount of iron equivalent to the total acidity of the solution was dissolved within 3 days at most. Then followed a slow, steady, and very slight loss due to 'rusting' (oxidation by dissolved oxygen or water itself). In inks, the time required to reach the maximum was slightly greater. This was followed by a gradual loss which was independent of the original acid concentration, but of greater extent than the rusting noted in the experiments with acids. The loss was caused by the action of the tannic and gallic acids. This observation was confirmed in another experiment in which tannic and gallic acids alone were used in the solution."

Rupert also designed a simple apparatus for making a corrosion test, by alternately dipping the pens into the ink, hanging them in the air to dry, again dipping, and so on as long as desired. By this method the building up of a deposit on the pens could be observed. Many persons regard this deposit of dried and more or less oxidized ink as evidence of corrosion, though it may not be.

The surface area has no direct connection with the weight of the pens, so the loss in weight is stated in milligrams, and not as a percentage. The test is at best a crude one, and the results of duplicate determinations do not check one another very closely.[21]

As a rule, all parts of the pens seem to be equally attacked by the ink, but now and then a strikingly different type of corrosion is met with. In this, the attack is chiefly at the edges, including those of the open slot and of the slits. Pens have been seen with their central slits opened to a width of nearly a millimeter (one twenty-fifth of an inch). This effect, which seems not to have been mentioned in print elsewhere than in the immediate predecessor of this circular, is due to the ink, because both pens are always affected in the same way and to the same extent in a given ink. The effect has never been noticed with the standard ink. A possible reason is that the ink contains an acid that is barely able to dissolve iron, so its action is limited to the parts of the pens that have undergone the most severe mechanical treatment. This, of course, is where the metal has been cut.

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[20] F. F. Rupert, Ind. Eng. Chem. **15**, 489–493 (1923).

[21] Mitchell and Hepworth, in the third edition of their book (see footnote 1), say on page 162: "This method, which the writer [presumably Mitchell] devised some years ago and published in the first edition of this book, has recently been included in the United States specifications without acknowledgment." On page 123 of the first edition of the book (1904) the following is found: "Another practical test is to immerse a pen in the ink for a given period, and to determine the loss in weight. Thus in the case of the ink referred to above we found that a pen had lost 5.18 percent of its weight after being kept in 10 cc of the ink for a month, whilst the ink itself had become nearly solid." The germ of the method in the specification may have come from the book, but at least as long ago as 1907 the test had been developed to its present form, which differs in several details from the procedure of Mitchell and Hepworth.

Other ways of determining the corrosiveness of inks have been suggested.[22] The most unexpected is that of Schluttig and Neumann, who said:

> We can be sure that an ink which darkens as quickly and intensely as the type [standard] can not contain relatively too much free acid—relatively only, for according to the quantity of iron salts the permissible degree of acidity will be greater or less, naturally only within narrow limits.

2. RED INK

Red ink is much simpler to test than blue-black ink. It is examined for sediment in the same way, and is judged more strictly from that standpoint, for a manufacturer has no excuse for failing to make a clear solution of a dye, and the solution when made should remain clear. Ink that is cloudy when received should be rejected without being tested, unless perhaps it has been chilled in transit. In that case it should be allowed to come to room temperature, to see whether it will become clear, though this rarely happens.

Streaks are made on paper, and are subjected to the light-fading test, but for only 24 hours, instead of 48 as for blue-black inks. In red ink, pens corrode hardly more than they do in distilled water. The loss in weight of a pair of pens immersed in red ink for 48 hours will rarely be as much as 10 mg.

3. STAMP-PAD INK

Stamp-pad inks dry almost entirely by soaking into the paper on which the impressions are made. That they can not dry to any great extent by evaporation is evident from the fact that they contain a large proportion of glycerin, which tends to absorb moisture from the air and is practically nonvolatile at ordinary temperatures. It is used in order to keep the ink from drying on the inking pad.

For testing, small stamp pads are made by cutting disks of white felt about 6 mm (¼ inch) thick and 38 mm (1½ inches) in diameter. The easiest way to cut them is by means of a brass tube of the required diameter, which is sharpened at one end, like a cork borer. These disks fit snugly inside of rings cut from brass tubing. A pad made in this way works quite as satisfactorily as the more complicated arrangement described in the Federal specification. The pads are placed upon a pane of glass, partly for cleanliness, but also to prevent the loss of ink that would occur if they rested upon paper or unpainted wood. Equal volumes of the sample and of the standard ink of the same color are placed upon separate pads. Impressions are made with both inks upon the same sheet of white bond paper, with a clean rubber stamp. The impressions made with the sample should dry as rapidly as those made with the standard, and should be as sharp and as intensely colored. Impressions made with each ink are exposed at a distance of about 10 inches from a glass-enclosed carbon arc for 24 hours. The sample should fade no more than the standard.

The inked pads are allowed to stand exposed to the air for 10 days. At the end of that time, the sample should show no more evidence of absorption of excessive moisture from the air, or of drying and caking on the pad, than does the standard.

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[22] Mitchell and Hepworth, p. 163 of their third edition; see also Analyst **46**, 131 (1921). Schluttig and Neumann, p. 77–78. Rupert, Ind. Eng. Chem. **15**, 489–493 (1923).

4. INDELIBLE MARKING INK FOR FABRICS

There is no formula for a standard ink in the Federal specification for indelible marking ink for fabrics. The tests are intended to represent severe treatment in a laundry, and also to find out whether the ink weakens, or "tenders", fabrics. The first step is to prepare inked strips of cloth for the tendering test. Strips 4 inches wide and 36 inches long are cut in both the warp and the filling directions from suitable closely woven cotton or woolen cloth, whichever the ink is intended for. Each strip is cut into test pieces 6 inches long. Across half of the test pieces representing each direction of the weave, the ink is applied in a band about 1 inch wide. The remaining test pieces are left uninked. After 10 days, the breaking strengths of the inked and uninked pieces are determined in a suitable machine. The breaking strength of the inked fabric must then be not less than 90 percent of the breaking strength of the uninked fabric.

On other pieces of suitable fabric, marks are made with the ink, strictly in accordance with the manufacturer's directions. Some of the marked pieces are kept for 2 weeks, and are then examined for any discoloration beyond the limits of the actual marks.

Two or three of the marked pieces are put through a series of washing tests in solutions prepared as follows:

Soap solution.—Dissolve 7 g of white floating soap and 7 g of modified soda (58 percent of sodium carbonate and 42 percent of sodium bicarbonate) in enough distilled water to make the volume of solution 1 liter.

Oxalic acid.—Dissolve 6 g of crystallized oxalic acid in 1 liter of commercial 28-percent acetic acid.

Sodium bisulphite.—Dissolve 5 g of sodium bisulphite and 72 ml of hydrochloric acid of specific gravity 1.11 in enough distilled water to make 1 liter.

Bleaching solution.—Prepare a solution of bleaching powder, and dilute so that it contains 1.4 percent of available chlorine. For use, 100 ml of this stock solution is diluted with 1,300 ml of distilled water.

All the washing tests are made with the solutions at 65 to 71° C (149 to 160° F). The marked pieces are immersed in the soap solution for 15 minutes, then rinsed 5 times with distilled water, and dried. These operations are performed 6 times. The same pieces are then treated similarly, and 6 times each, in the oxalic acid for 10 minutes, the sodium bisulphite for 10 minutes, and in the bleaching solution for 5 minutes. The marks must be clearly readable after the 24 washings.

5. BLACK AND COLORED DRAWING INKS

The Federal specification for black waterproof drawing ink depends chiefly upon practical tests. Lines of different specified widths are drawn upon white drawing paper and upon tracing cloth. With the slit of the drawing pen set at a width of 0.003 inch, it must be possible to draw five lines, each 6 inches in length, at intervals of 5 minutes, "without extraneous assistance to promote the flow of ink." With the slit at a width of 0.012 inch, a set of lines shall be drawn and then, before they are dry, a second set shall be drawn across them at right angles. The ink shall be regarded as unsatisfactory if the intersections of the lines are not clean and sharp. Lines drawn with the slit of the pen set at 0.012 inch shall be tested for smudging or blurring, by rubbing them with a dry fingertip 5 minutes after they are drawn. These lines shall be further tested by cutting the tracing cloth and paper into strips, and soaking one strip of each in water, gasoline, benzene (benzol), and carbon tetrachloride for 1 hour. After drying, the soaked lines shall show no evidence of bleeding, running, or smearing. To determine the resistance of the ink to the growth of mold, a portion of it shall be inoculated with the spores of the common green mold, and then kept in a dark, moist place, at about 30° C (86° F) for 14 days.

It is specified that the ink shall not contain synthetic dyes. To test for them, mix 2 ml of the ink with 20 ml of alcohol to which 5 or 6 drops of glacial acetic acid has been added. The carbon flocculates in a few minutes, and is then filtered off, washed with a little alcohol, and dried at room temperature. The clear filtrate from the carbon shall not have more than a trace of color. A colorless filtrate is only contributory evidence, not proof, that dye is absent. It may have been carried down with the carbon and the waterproofing material—probably shellac—when the ink was mixed with the acidified alcohol. So the dried precipitate is tested with caustic soda solution, concentrated sulphuric acid, and other reagents commonly used for the detection of dyes. Any change in the color of the precipitate, or the production of strong, characteristic colors in the reagents shall be regarded as proof of the presence of dye in the ink.

Although there is no formula for a standard black drawing ink, colored waterproof drawing inks are tested, in part, by comparison with inks made as described in section III,4. The seven "first choice" dyes are used for making the standards.

Lines are drawn on drawing paper and on tracing cloth, with the slit of the pen set to widths of 0.003 and 0.02 inch. There shall be no noticeable difference in the intensity or the shade of color between the fine and the heavy lines. The dried lines shall not be blurred nor smudged when they are rubbed with a dry fingertip. When soaked, as described for black drawing ink, in water, gasoline, benzene (benzol), and carbon tetrachloride, the ink shall show no evidence of running, bleeding, smearing, or bleaching. The ink is tested for resistance to the growth of mold; and the fastness of the color, when the lines are exposed to the light of a glass-enclosed carbon arc, shall be determined. Black ink is so exposed for 48 hours, and colored ink only 12 hours.

V. APPENDIX

1. WEIGHTS AND MEASURES

Metric weights and measures are so simple in principle and in their interrelations that they are used in most of the formulas in this circular. As many readers will prefer ordinary weights and measures, some conversion factors and other pertinent information are given.

The standard unit of weight in the metric system is the kilogram (kg), or 1,000 g; and the unit of capacity is the liter, or 1,000 ml, which is the volume occupied by 1 kg of pure water at the temperature of its greatest density, and under a pressure of a normal atmosphere. According to the original intent, the kilogram was to have been the mass of 1,000 cubic centimeters (cm^3) of water at its greatest density, and a liter would then have been 1,000 cm^3. This relation was not realized, on account of experimental difficulties, and it is now known that instead of being 1,000.000 cm^3, the actual volume of the liter is 1,000.027 cm^3. The difference, equal to the volume of a small drop of water, is negligible in most chemical work. Many laboratories still cling to the name cubic centimeter for the volume called milliliter (ml) throughout this circular.

Water expands when heated, and thus its density, or mass per unit volume, decreases. The change is small for ordinary temperature ranges, and for practical purposes not requiring great accuracy, the weight of both 1 liter and 1,000 cm^3 can be called 1 kg; and 1 ml and 1 cm^3 will weigh 1 g. So if a formula calls for 50 g of water, it will be sufficiently accurate to take 50 ml.

If it is desired to measure other liquids than water, instead of weighing them, their specific gravities must be considered. For instance, if 35.4 g of concentrated sulphuric acid is required, that figure must be divided by 1.84, the specific gravity of the acid. The volume will be 35.4/1.84, or 19.2 ml. The rule is the same for liquids lighter than water. Thus, 80 g of acetone, of specific gravity 0.79, will equal 80/0.79, or 101.3 ml.

Liquids pack perfectly without air spaces, so it is safe to measure, instead of weighing, them. This is not true of solids, because the weight of a powder that a given measure will hold depends not only upon the density of the solid particles, but also upon their size and shape, and how closely they are packed together. The specific gravity of the solid particles is not always the most important factor in the weight of a given bulk of them, as an illustration will show. The oxide of lead known as litharge has a specific gravity that varies somewhat according to the method of preparation, but it is usually a little above 9. Some determinations were made of the weight of a sample of unusually fine-grained litharge that could be packed into the space of 1 cubic inch (16.39 cm^3). Taking the specific gravity as 9, a cubic inch of litharge in one solid piece would weigh $9 \times 16.39 = 147.5$ g. The weight of the fine powder that could be packed into the cubic-inch measure was about 35 g, or 112.5 g less than a solid cubic inch would weigh. In other words, the air between the particles of litharge occupied 112.5/147.5, or about 76 percent of the cubic inch. The apparent specific gravity of the powder was $35/16.39 = 2.14$.

The conversion factors about to be given are based upon accurate comparisons of the kilogram and the avoirdupois and the apothecaries' pounds, and of the liter and the United States gallon. The avoirdupois pound is 16 ounces, and the apothecaries' pound, 12 ounces. These ounces are quite different, as the tables show. Hence the weights of the two pounds are not in the ratio 16:12, but more nearly as 12:10.

Metric and Avoirdupois Weights

1 kg=2.2046 pounds=35.274 ounces.
1 g=0.001 kg=0.0353 ounce=15.43 grains.
1 pound=0.45359 kg=453.59 g=7,000 grains.
1 ounce=28.35 g=437.5 grains.

Metric and apothecaries' weights

1 kg=2.6792 pounds=32.151 ounces.
1 g=0.0322 ounce=15.43 grains.
1 pound=0.37324 kg=373.24 g=5,760 grains.
1 ounce=31.103 g=480 grains.

Metric and United States measures

1 liter=0.2642 gallon=1.0567 quarts=33.81 fluid ounces.
1 ml=0.001 liter=0.0338 fluid ounce.
1 gallon=128 fluid ounces=3.7853 liters.
1 quart=32 fluid ounces=0.9463 liter=946.3 ml.
1 fluid ounce=29.57 ml.
1 liter of water weighs 1 kg, or 1,000 g.
1 gallon of water weighs 8.33 avoirdupois pounds, or 10.12 apothecaries' pounds.
1 fluid ounce of water weighs 1.04 avoirdupois ounces, or 0.95 apothecaries' ounce.

If the weight of a gallon of water is calculated from the factors for converting kilograms to pounds and gallons to liters, or 2.2046×3.7853, the result is 8.345 avoirdupois pounds. This differs from the value, 8.33 pounds, in the table. The reason is that the factors are determined at 4° C (39.2° F), at which temperature the density of water is greatest. So at any other temperature than 4° C, a measured gallon of water (231 cubic inches) will weigh less than 8.345 pounds.

To find the weight at any temperature, multiply the density of water at that temperature by 8.345. Suppose the gallon of water is measured at 20° C (68° F). At this temperature the density of water is 0.99823, and $0.99823 \times 8.345 = 8.330$ avoirdupois pounds. For ordinary work at any "room temperature", as chemists so often say when the exact temperature is of no importance, 8.33 avoirdupois pounds is sufficiently accurate.

The British, or imperial, gallon holds 10 avoirdupois pounds of water, and is therefore 1.200 times the United States gallon; and the latter is 0.833 imperial gallon. So, for instance, 1 imperial quart is $0.9463 \times 1.200 = 1.1356$ liters; and 1 liter is $1.0567 \times 0.833 = 0.8802$ imperial quart.

The figures to the right of the decimal points can not be ignored in making calculations, but when it comes to actually weighing or measuring the materials for a liter of ink, even the first decimal figure may be of little importance. At the same time it must be remembered that kitchen scales are not suitable for weighing grams, nor a battered quart cup for measuring milliliters. It will not do to be too haphazard when making the standard ink of a specification.

The use of the conversion factors will be seen from the following example: Suppose it is desired to make 125 gallons of the standard red ink, which contains 5.5 g of dye in a liter. One g equals 0.0353 avoirdupois ounce, and 1 liter equals 1.0567 quarts. Then 1 g in a liter equals $0.0353/1.0567 = 0.0334$ ounce in a quart;[23] and 5.5 g in a liter will be $0.0334 \times 5.5 = 0.1837$ ounce in a quart. This last figure multiplied by 4 to get the fraction of an ounce in a gallon, and then by 125 to get the weight of dye for 125 gallons, gives 91.85 avoirdupois ounces, or 5.74 pounds of dye.

2. EQUIPMENT FOR MAKING INK

The manufacturer of inks will have proper equipment, but whoever makes small batches at home must put up with makeshifts, unless he has some chemical glassware for preparing the solutions, a measuring cylinder or two, and moderately sensitive scales with small weights. Usually the weights are apothecaries', but metric weights can be obtained. Dealers in photographic supplies sell scales for those who make their own developing and fixing solutions.

If ordinary bottles must be used, instead of laboratory ware, and the solutions have to be heated, there are two safe ways to go about it. One is to set the bottle in a deep vessel containing cold, or at most lukewarm, water, and then to pour in hot water slowly, and not against the side of the bottle. Another way is to set the bottle in water as before, but to put under it a piece of wire netting or a spiral of heavy wire to keep the bottle from touching the bottom of the vessel. It can then be heated over a low gas flame or on a stove. The idea in either case is not to heat the outside of the bottle too quickly while its contents are cold, because the expansion due to the heat may so strain the glass that it will break. The materials will dissolve more quickly if the bottle is swirled or shaken frequently so as to stir up the relatively concentrated solution at the bottom.

So far as possible, avoid the use of metal vessels for making ink. Iron, especially, should not be used, because it is acted upon so easily by acids, and may also cause discoloration of some dyes.

3. DYES FOR MAKING INK

Not all dyes are equally suitable for making inks, and in the formulas in this circular, various dyes have been recommended. In each case the name of the dye is followed by certain letters and number in parenthesis, as "Soluble blue (C.I. 707; Sch. 539)." An explanation of these symbols is in order.

There are many more dye names than there are different kinds of dyes because manufacturers like to use names of their own choice for their products. As a rule, the more widely a dye is used, the more apt it is to have a great many names. At least a dozen names have been given to the familiar dye, bismarck brown. This practice of multiplying names is enough to cause confusion, and the situation is further complicated by the fact that nearly or quite the same name may be

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[23] Those who prefer multiplication to division can start with the relation 1 quart equals 0.9463 liter. Then $0.9463 \times 0.0353 = 0.0334$ ounce, as before.

given to dyes that differ in chemical composition and structure. Thus, there are several "fast reds" and "soluble blues." It is true that some attempt is made to distinguish between different dyes that have the same name by adding letters, or numerals and letters, for instance, toluylene orange *G* and toluylene orange *R*. This plan might be better if there were not so many letters to choose from, and so many possible combinations of them. To give an example, a certain dye has been called erythrosine, and erythrosine followed by *D*, *B*, *J*, *JNV*, or *W*, to say nothing of seven other quite different names that have been given it. Again, sometimes a manufacturer will sell the identical dye under two or more brand names.

To do away with this sort of confusion, two important tabulations of dye names have been published. The first is Gustav Schultz's "Farbstofftabellen" (Dyestuff Tables), of which there have been several editions. The second is the "Colour Index" of the British Society of Dyers and Colourists. In each book the dyes are arranged in groups, according to the type to which they belong, and are further classified according to their chemical formulas in each group. The dyes are numbered serially, so any one number applies to only one dye. Thus, 707 in the Colour Index means a particular dye, one of the soluble blues, and nothing else. The same dye is no. 539 in Schultz's book. It will now be understood by the reader that such a symbol as (C.I. 707; Sch. 539) is the most certain way of telling the seller just what kind of dye is wanted.

The Year Book of the American Association of Textile Chemists and Colorists gives the names by which the various types of dyes made in this country are known by the manufacturers. Usually there are several names for each type, in which case the year book gives a preferred name. With one or two exceptions, the dye names given in table 3 are the preferred names in the year book. A few alternative names are also given in the list. Many more dyes than those in the list can be used for making inks. The list is given as an aid to readers who would otherwise have no idea what to ask for.

TABLE 3.—*Dyes for various inks*

RED DYES

	Colour Index number	Schultz number
Fast crimson	31	42
Azorubine (nacarat *S*)	179	163
Crocein scarlet *3B* (crocein scarlet *MOO*)	252	227
Benzo fast scarlet	326	279
Congo red	370	307
Benzopurpurine *10B*	495	405
Fuchsine (magenta)	677	512
Rhodamine *B*	749	573
Erythrosin, yellowish	772	591
ORANGE DYES		
Crocein orange	26	37
Brilliant orange *R*	78	79
Orange *R*	161	151
Orange *TA*	374	311
Toluylene orange *R*	446	362
Toluylene orange *G*	478	392
Pyrazol orange	653	----------
YELLOW DYES		
Naphthol yellow	10	7
Metanil yellow	138	134
Brilliant yellow	364	303
Tartrazine	640	23
Auramine	655	493
Thiazol yellow	813	198
Chloramine yellow	814	617

Table 3.—*Dyes for various inks*—Continued

GREEN DYES

	Colour Index number	Schultz number
Chloramine green *B*	589	470
Diamine green *B*	593	474
Malachite green (victoria green)	657	495
Emerald green	662	499
Brilliant milling green *B*	667	503
Light green *SF*	670	505

BLUE DYES

	Colour Index number	Schultz number
Naphthol blue-black *S* (agalma black *10B*)	246	217
Benzo cyanine *R*	405	336
Benzo blue *2B*	406	337
Diamine sky blue *FF* (direct sky blue *6B*)	518	424
Benzo sky blue (direct sky blue)	520	426
Soluble blue (bavarian blue *DSF*)	705	537
Soluble blue	707	539
Victoria blue	729	559
Wool blue *G* extra	736	565
Methylene blue	922	659
New methylene blue *N*	927	663
Indigotin (indigo; indigo carmine)	1,180	877
Prussian blue	1,288	968

VIOLET DYES

	Colour Index number	Schultz number
Diamine violet *N*	394	327
Oxamine blue *4R* (Erie violet *4R*)	471	385
Hofmann's violet	679	514
Methyl violet *B*	680	515
Crystal violet	681	516
Acid violet	698	530

BROWN DYES

	Colour Index number	Schultz number
Bismarck brown *R*	332	284
Benzamine brown *3GO*	596	476
Benzo brown *G*	606	485

BLACK DYES

	Colour Index number	Schultz number
Durol black *B*	307	265
Columbia fast black *FF* (diamine fast black *FF*)	539	436
Direct deep black *RW*	582	463
Nigrosine base	864	698
Nigrosine, water-soluble	865	700

In the two Federal specifications for iron gallotannate inks, the blue dye that must be used in the standard inks is the particular soluble blue designated as C.I. 707. According to the Colour Index, this dye is derived from a mixture of triphenylpararosaniline and diphenylrosaniline. These two dyes are insoluble in water, but dissolve readily when converted into the mixture of the trisulphonic acids, or of some of their salts. Because this conversion is never complete, the dye always contains some of the disulphonic, or even of the monosulphonic, acids. The acids are not used as such, but are converted into their sodium, ammonium, or calcium salts. The calcium salts of the mono- and di-acids are nearly insoluble in water, and for that reason some manufacturers make the calcium salts when the dye is for use in ink. For two reasons it is less profitable to sell the calcium instead of the sodium salts. First, the mono- and disulphonic acids cannot be sold mixed with the trisulphonated product. In the second place, considering the atomic weights and the valences, a given weight of the acid will yield a somewhat greater weight of the sodium than of the calcium salt. Schluttig and Neumann used bavarian blue *DSF*, which is the sodium salt of the disulphonic acid of triphenylpararosaniline, mixed with more or less of the monosulphonate.

Both tannin and iron salts are used as mordants in dyeing. That is, they form insoluble compounds with some kinds of dyes, and thus serve to fix them upon the fabric. Because of the composition of iron gallotannate inks, by no means all classes of dyes can be used in them. The dye must be of a type that does not form an insoluble compound with anything else in the ink. Also, because sometimes a factory batch of soluble blue is not sulphonated as it should be, it is advisable when buying to specify that the dye must be "for ink." A reliable dealer will then not supply soluble blue that is satisfactory for ordinary uses, but not for making ink. The new formulas in section II, 5 (e) require exceptionally good dye, and there may be some difficulty in getting it. Unfortunately there are no laboratory tests, aside from making ink and testing it, by which it can be determined whether the dye is of the desired quality. With suitable dye, the new inks should show greater stability in the sediment test than the standard blue-black writing ink.

A few dyes that are more or less satisfactory substitutes for soluble blue are naphthol blue-black *S* (C.I. 246; Sch. 217), benzo blue *2B* (C.I. 406; Sch. 337), diamine sky blue *FF* (C.I. 518; Sch. 424), and benzo sky blue (C.I. 520; Sch. 426). Acid black *N* (C.I. 294; Sch. 261), when used at the rate of 3.5 g in a liter, has nearly the same shade of color as soluble blue. Two dyes that caused rapid deposition of sediment were durol black *B* (C.I. 307; Sch. 265) and direct deep black *RW* (C.I. 582; Sch. 463). These remarks apply only to the use of the dyes in iron gallotannate ink. The dyes have not been tested in iron gallate ink.

In addition to bavarian blue, Schluttig and Neumann named three other dyes which they used for matching the exact shades of inks submitted to them for test. Apparently these inks had a wide range of colors, because they used red, brown, and green dyes. Their red dye was azorubine, which they called nacarat *S* (C.I. 179; Sch. 163). The green dye was guinea green *B* (C.I. 666; Sch. 502), which they knew as acid green *VBSPo*. Their "Kastanienbraun" (chestnut brown) cannot be found in the Colour Index nor in Schultz's Farbstofftabellen. The chestnut brown of the Colour Index is umber, not a dye at all, but an insoluble earth used as a pigment.

In making dyes, it is often necessary to salt them out of solution; that is, to precipitate them by dissolving common salt in a concentrated solution of the dye. When this must be done, the dye unavoidably contains more or less salt. Many dyes also are intentionally mixed with salt or some other uncolored substance to dilute them to the strength with which dyers have long been familiar, because the formulas furnished by the manufacturers are based upon these diluted dyes. This is a recognized trade practice that is not to be regarded as adulteration. For making inks it is preferable to have the concentrated forms of the dyes, and these should be ordered from the manufacturer, even though they cost more.

4. LITERATURE ON INKS

This circular gives only a few of the very numerous published formulas for inks. Every public library has books in which other formulas can be found, as well as references to still other books and to articles that have appeared in scientific and technical journals. There is no dearth of reading matter relating to inks, and the list given here is by no means complete.

1. A. H. Allen, Commercial Organic Analysis, 5th ed., **5**, 205–267 (P. Blakiston's Son & Co., Philadelphia, 1927).
2. H. Bennett, Practical Everyday Chemistry (The Chemical Publishing Co., New York, N. Y., 1934).
3. H. Bennett, The Chemical Formulary, 3 vol. (D. Van Nostrand Co., New York, 1933–1936).
4. W. T. Brannt and W. H. Wahl, Techno-Chemical Receipt Book (H. C. Baird & Co., Philadelphia, 1905).
5. D. Carvalho, Forty Centuries of Ink (Banks Law Publishing Co., New York 1904).
6. Henley's Twentieth Century Book of Recipes, Formulas, and Processes (Norman W. Henley Publishing Co., New York, 1928).
7. J. B. Lavay, Disputed Handwriting (Harvard Book Co., Cambridge, Mass., 1909).

8. S. Lehner, Manufacture of Inks (Translated, with additions, by W. T. Brannt, H. C. Baird & Co., Philadelphia, 1892).
9. C. A. Mitchell and T. C. Hepworth, Inks, Their Composition and Manufacture, 3d ed. (Chas. Griffin & Co., (Ltd.), London, 1924).
10. A. S. Osborn, Questioned Documents (Lawyers' Cooperative Publishing Co., Rochester, N. Y., 1910).
11. J. H. Oyster, Spatula Ink Formulary (Spatula Publishing Co., Boston, 1912).
12. O. Schluttig and G. S. Neumann, Die Eisengallustinten (The Iron-Gall Inks) (v. Zahn & Jaensch, Dresden, 1890).
13. Scientific American Cyclopedia of Formulas. Edited by A. A. Hopkins (Munn & Co., New York, 1921).
14. E. Spon, Workshop Receipts (E. & F. N. Spon, London and New York, 1917).
15. N. Underwood and T. V. Sullivan, Chemistry and Technology of Printing Inks, (D. Van Nostrand Co., New York, 1915).
16. F. B. Wiborg, Printing Ink (Harper & Bros., New York, 1925).

Articles in chemical journals are:

L. S. Munson, *The testing of writing inks*, J. Am. Chem. Soc. **28**, 512–516 (1906).
F. F. Rupert, *Examination of writing inks*, Ind. Eng. Chem. **15**, 489–493 (1923).
E. W. Zimmerman, *Colored waterproof drawing inks.* Ind. Eng. Chem. **25**, 1033 (1933).
C. E. Waters, *Blue dye as evidence of the age of writing*, Ind. Eng. Chem. **25**, 1034 (1933).

A few publications of the National Bureau of Standards relate to inks. The Federal specifications, formerly issued as circulars of the Bureau, are now parts of the Federal Standard Stock Catalog, and are no longer distributed by the Bureau. Many public, college, and university libraries throughout the country have the publications of the Bureau, and possibly also the specifications, as well as publications from other branches of the Government. Those that are in print can be bought from the Superintendent of Documents, United States Government Printing Office, Washington, D. C., for the prices stated. Postage stamps will not be accepted, and money is sent at the purchaser's risk. Postal money orders, or coupons sold by the Superintendent of Documents in sheets of 20 for $1, are accepted. The coupons are good until used. In ordering, the name of the Bureau as well as the title and number of the publication should be given.

The letter circulars mentioned below are mimeographed, and are not handled by the Superintendent of Documents, but orders for all other publications should be addressed to him.

J. B. Tuttle and W. H. Smith, Analysis of Printing Inks, BS Tech. Pap. 39 (1915). (Out of print.)
Composition, Properties, and Testing of Printing Inks, BS Cir. 53, 1915. (Out of print.)
Inks—Their Composition, Manufacture and Methods of Testing. Cir. BS C95, 1st ed. (1920). (Out of print.)
Inks, Typewriter Ribbons and Carbon Paper. Cir. BS C95, 2d ed. (1925). (Out of print.)
Inks, Cir. BS C400 (1933). (Superseded by C413.)
P. H. Walker, Some Technical Methods of Testing Miscellaneous Supplies. Misc. Pub. BS M15 (1916). A reprint, with notes and corrections, of Bur. Chemistry, Dept. Agr. Bul. 109, (1912). The methods differ considerably from those of the Federal specifications. (Out of print.)
A. E. Kimberly and B. W. Scribner, Summary Report of Bureau of Standards Research on Preservation of Records. Misc. Pub. BS M144 (1934). (Out of print.)
E. W. Zimmerman, C. G. Weber, and A. E. Kimberly, *Relation of ink to the preservation of written records.* J. Research NBS **14**, 463–468 (1935), RP779. 5c.
E. W. Zimmerman, *Iron gallate inks—liquid and powder.* J. Research NBS **15**, 35–40 (1935) RP807. 5c.
C. E. Waters, *Inks for recording instruments.* J. Research NBS **17**, 651 (1936) RP935. 5c.
Dry Etching of Glass. BS Letter Circular LC150. Free.
Carbon Paper and Typewriter Ribbons. BS Letter Circular LC424. Free.
Stain Removal from Fabrics: Home Methods. U. S. Dept. Agr. Farmers' Bul. 1474 (1930). 5c.
B. L. Wehmhoff and D. P. Clark, Standard Mimeograph Ink and Paper. U. S. Govt. Printing Office Tech. Bul. 15 (1932). Free.
B. L. Wehmhoff, D. P. Clark, and D. H. Boyce, Newsprint and News Ink, U. S. Govt. Printing Office Tech. Bul. 18 (1933). Free.

The following Federal specifications are sold separately by the Superintendent of Documents for 5c apiece:

TT–I–521, Ink; copying and record.
TT–I–528, Ink; drawing, waterproof, black.
TT–I–531, Ink; drawing, waterproof, colored.
TT–I–542, Ink; marking, indelible (for) fabrics.
TT–I–549; Ink; red.
TT–I–556, Ink; stamp-pad.
TT–I–563, Ink; writing.

WASHINGTON, October 2, 1936.

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