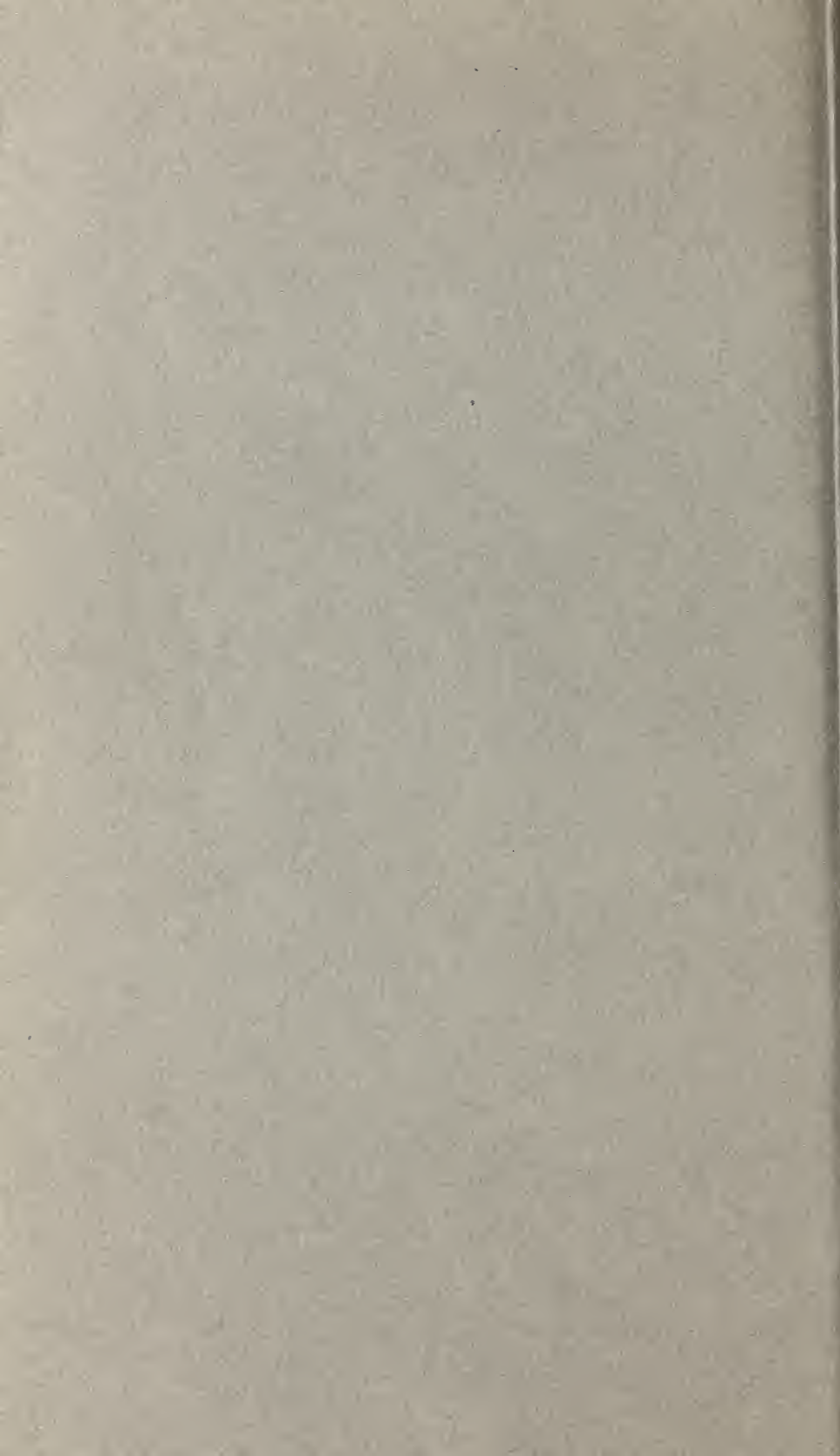


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**U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS**

# **I N K S**

**CIRCULAR C426**



U. S. DEPARTMENT OF COMMERCE  
HARRY L. HOPKINS, Secretary  
NATIONAL BUREAU OF STANDARDS  
LYMAN J. BRIGGS, Director

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CIRCULAR OF THE NATIONAL BUREAU OF STANDARDS C426

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# INKS

By C. E. WATERS

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## PREFACE

Since 1906, when the National Bureau of Standards began to test inks, a surprisingly large number of persons have written for all sorts of information about them. Because it is not feasible to give a great deal of detailed information in a letter, in 1920 the Bureau published Circular C95, *Inks—Their Composition and Manufacture*. The second edition, in 1925, was called *Inks, Typewriter Ribbons, and Carbon Paper*. These circulars gave very few formulas, and because so many letters asked how to make inks, Circular C400, *Inks*, with 50 or more formulas, was published late in 1932. There proved to be a great demand for this circular, and in 4 years more than 2,600 copies of it were distributed. A revised and somewhat enlarged edition, C413, with the same title, was published in December 1936, since which date over 2,400 copies have been distributed.

The present circular is a thoroughly revised and considerably enlarged edition of C413. It contains new formulas and takes up topics which do not appear in C413. 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 iron gallate inks, discusses the aging of writing, the restoration of faded writing, the freezing of inks, and the effect of inks upon paper. After this come short discussions, with formulas, of other kinds of inks, including colored writing inks, drawing, stamp-pad, recording-instrument, and others.

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, with conversion factors, on equipment for making ink in the home, and on dyes suitable for making inks. Finally, there is given a short list of selected literature references.

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## 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 use to mark an unfamiliar trail. The spirited though crude drawings left on the walls of European caves by men of an earlier culture than ours show that primitive man was akin to us. Worse art is to be seen today on the walls of 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 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 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 used for 3,000 years, are prepared by making lampblack into a stiff paste with a solution of glue, gelatin, or some plant gum 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 in early days 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 suggested are those by Mitchell<sup>1</sup> and by Carvalho.<sup>2</sup> It may be mentioned in passing that Mitchell gives an interesting illustrated account of the Chinese process for the manufacture of India ink.

## 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 sulfate (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 to the bottom, and the solution could blacken. The change in color was caused by the action of oxygen of the air on 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 nearly insoluble in water. Ink made by this process was a muddy fluid in which floated innumerable microscopic particles of the black compound of iron and tannin. The glue

<sup>1</sup> C. A. Mitchell, *Inks, Their Composition, and Manufacture*, 4th ed. (J. B. Lippincott Co., Philadelphia, Pa., and New York, N. Y., undated, but probably 1937). T. C. Hepworth was joint author of the earlier editions.

<sup>2</sup> D. N. Carvalho, *Forty Centuries of Ink* (The Banks Law Publishing Co., New York, N. Y., 1904).

or the plant gum helped to keep the particles from settling to the bottom of the fluid, and later served to fasten them to 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 tannin. Even in his time there were no analytical procedures to help him, but although he had to work by cut-and-try methods, 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 sulfate, 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 the libraries of Europe. More about this will be found in section II, 13.

## 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 become oxidized and turned into a muddy fluid, it was guarded from the action of the air, and kept free from sediment 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 and insoluble. For this reason it can be argued that 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 contain a small quantity of free acid, usually hydrochloric or sulfuric acid, to retard oxidation and to hold in solution the black iron compound, whose formation cannot be avoided entirely. The more free acid the ink contains, the longer will it remain clear, but the greater will be its corrosive action on steel pens, and if the acid is sulfuric, the greater will be its destructive effect upon paper. There must be some sort of compromise, if the use of iron gallotannate inks 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 noncorrosible point puts a temptation in the path of the ink maker, who knows that the addition of a little more acid will make his ink stay clear longer on the retailers' shelves.

A solution of ferrous iron and tannin which has undergone but a little oxidation does not look intensely black in the bottle, and the marks it makes on paper are very pale, though in a few days they become black. To make this solution acceptable as ink it is necessary to give it a stronger color by the addition of a dye. When clear iron gallotannate inks were first made, the synthetic, or so-called aniline, dyes were 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 the solid matter in the ink. Indigo itself is not soluble, but by suitable treatment with strong sulphuric acid it is converted into indigodisulfonic 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,<sup>3</sup> because of its far-reaching and lasting influence. 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 and with unchanged punctuation, is here given:

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 and 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 which 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 iron inks made with substances which 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, in the following section.

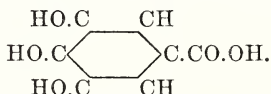
<sup>3</sup> O. Schluttig and G. S. Neumann, *Die Eisengallustinten* (The Iron-Gall Inks) p. 7 and 8. (v. Zahn & Jaensch, Dresden, Germany, 1890).

Before coming to that, a bit of history may be recounted. Schluttig and Neumann say that the first iron-gall ink made in Germany, which possessed all the properties required today of a good ink, was the so-called "alizarin ink", which Aug. Leonhardi, their employer, patented in Saxony and most of the European countries. This name was given because at first this ink contained alizarin, the coloring matter of madder. Alizarin was found to be unnecessary, and the ink was later made without it, but the name was not dropped. Leonhardi said he chose the name for the ink, "not to indicate its composition, but solely to designate my product as something new." S. Lehner<sup>4</sup> says: "In accordance with their name, these inks should contain alizarin. \* \* \* We do not know how this name originated; very likely it was arbitrarily chosen to deceive the public, and, if possible, also the chemist."

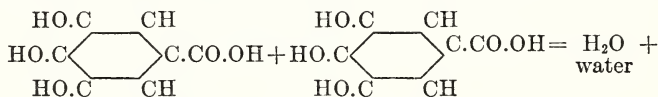
#### 4. TANNIN IN IRON GALLOTANNATE INKS

The tannins are a group of more or less closely related chemical compounds which are found in many different species 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 compounds of the familiar sugar, glucose (dextrose), with organic acids. The tannin in Chinese galls, a common raw material for making ink, is such a compound of tannic acid. Tannic acid is also called digallic acid, galloylgallic acid, and gallotannic acid. Three of these names indicate a relationship to gallic acid, which name in turn recalls the ultimate source, nutgalls.

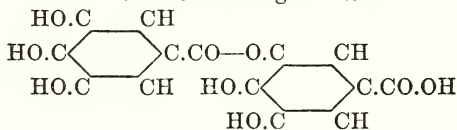
To the chemist, gallic acid is 3,4,5-trihydroxybenzoic acid, which means that it is benzoic acid,  $C_6H_5CO.OH$ , in which the hydrogen atoms in the 3, 4, and 5 positions with respect to the carboxyl,  $CO.OH$ , group are replaced by hydroxyl,  $OH$ . Because it is a derivative of benzene, the structural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



For convenience, the formula can be written:  $(HO)_3C_6H_2CO.OH$ . Gallic acid is both an acid on account of its carboxyl group, and an alcohol on account of having hydroxyl groups. Just as ethyl alcohol and acetic acid can react to form the ester, ethyl acetate, so two molecules of gallic acid can react to form the compound, tannic acid, which is both an ester and an acid. The equation makes this clear:



Two molecules of gallic acid



Tannic acid

<sup>4</sup>S. Lehner, *Manufacture of Inks*, translated, with additions, by W. T. Brannt. (H. C. Baird & Co., Philadelphia, Pa., 1892.)

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 experiments of Schluttig and Neumann in section II, 3. In addition to critically studying inks which contained different amounts and proportions of gallic and tannic acids, they made inks with 26 other substances which are chemically related to these two acids, but which differ from them in the number and arrangement of the hydroxyl and carboxyl groups attached to the benzene ring, or that have methoxyl, (OCH<sub>3</sub>), 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 acid, and these of all the substances studied made the best 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 they must be used in the correct amounts, or the ink will not be good. There should be no excess of 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 should be no deficiency nor excess of dye. The formula for "copying and record" ink in 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 United States Pharmacopoeia, in 1 liter of ink, to act as a preservative, as they put it. As we would now say, it was intended to serve as a "protective colloid" to hinder the precipitation of any ferric gallotannate formed in the ink by slow oxidation in the bottle. Some years ago the gum was omitted from the United States Government formula when proposals for bids were being typewritten. This clerical error was not discovered until it was too late to correct it, because the contract for a year's supply of ink had by that time been awarded. This led the then Bureau of Chemistry, United States Department of Agriculture, to make special tests of the ink prepared with and without gum arabic. These tests showed that the omission of the gum was an improvement, and ever since then it has been left out of the formula for the standard ink.

The Government formula calls for a dye which is different from the one recommended by Schluttig and Neumann, though closely related to it in composition. This is further discussed in section V, 3.

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. About 1930 the Commonwealth decided to leave gum arabic out of the formula, which is now the same as that in Federal Specification TT-I-521, for copying and record ink. A few years later in the 1890's, the Federal Government started to use the formula, and about 1914 Connecticut followed their lead. It



should be noted that Prussia, about 1912, decreed that the official ink should contain at least 4, and not more than 6, g of iron in a liter. Schluttig and Neumann made a series of inks which differed in their content of iron. They found that if the ink contained 4 g of iron in 1 liter, it gave "fairly black writing," and that with 6 g of iron the maximum blackness was attained. They recommended that ink for records should contain 6 g of iron in 1 liter. Three years before this, in 1887, a royal commission in Germany had decided that 4 g of iron sufficed.

The British specification for record ink requires that "it must reveal on analysis not less than 0.5 per cent. and not more than 0.6 per cent. of iron (calculated as metallic iron)."<sup>5</sup>

(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. This was published as Circular 182 of the National Bureau of Standards. It went out of print in 1930. Although it is not a true copying ink, it will make 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 was issued as Federal Specification TT-I-521, Ink; Copying and Record. The apparent subordination of "record" to "copying" is the result of alphabetical exigencies, to make the specification fit into what was considered its proper place in the Federal Stock 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 supplies. This impression is not in accord with the wording or the intent of the specification. Any manufacturer who has the knowledge and skill to use cheaper raw materials in making ink which meets the requirements of the specification may do so, but in order that both buyer and seller shall be able to make strictly comparable tests, their standard inks must be made of chemicals of the same definite degree of purity.

A standard ink is necessary because some of the requirements of the specification cannot be stated in exact terms, and also because some of the properties of the ink that are measured 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 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 Pharmacopoeia which is current at the time bids are asked for." This, however, does not apply to the dye, for which there is no commercial or other generally accepted standard.

<sup>5</sup> See p. 189 of the book cited in footnote 1.

*Standard Copying and Record Ink*

	<i>Grams</i>
Tannic acid.....	23. 4
Gallic acid crystals.....	7. 7
Ferrous sulfate crystals.....	30. 0
Hydrochloric acid, "dilute," U. S. P.....	25. 0
Carbolic acid (phenol).....	1. 00
Soluble blue (C. I. 707; Sch. 539) <sup>1</sup> .....	3. 5
Water to make a volume of 1 liter at 20° C (68 F).	

<sup>1</sup> The symbols in parenthesis, here and elsewhere in the circular, indicate definitely the type of dye intended. (See explanation in the discussion of dyes in the appendix.)

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

## (c) FORMER STANDARD FOR GOVERNMENT COPYING INK

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

*Former Standard Copying Ink*

	<i>Grams</i>
Tannic acid.....	46. 8
Gallic acid crystals.....	15. 4
Ferrous sulfate 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 <sup>1</sup> .....	5. 0
Water to make a volume of 1 liter at 20° C (68 F).	

<sup>1</sup> In those days, the dye was expected to be Bavarian blue *DSF*, which was recommended by Schluttig and Neumann. (See also sec. V, 3.)

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 Pharmacopoeia.

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

The formulas for copying and record ink and for the former copying ink call for the same amount of preservative (carbolic acid). The effectiveness of the preservative depends upon the quantity of it in a given volume of ink. Some persons have the idea that the preservative action of carbolic acid (phenol) consists in delaying the formation of sediment. It may do this indirectly, but the primary reason for adding phenol is to keep the ink from supporting the growth of bacteria and molds. Some of these organisms may cause the formation of sediment, but usually sediment results from the oxidation of ferrous to the less soluble ferric compounds. It is not known whether phenol has any effect upon the rate of oxidation of the ferrous compounds in ink. Phenol is easily oxidized, and it may well act as an antioxidant of the ferrous compounds, in the same way that various easily oxidized substances greatly prolong the life of rubber by delaying its oxidation. In this connection read what is said about the action of the dye on ink made by the formula for ferrous sulfate ink powder. (See sec. II, 6 (b).)

## (d) STANDARD FOR GOVERNMENT WRITING INK

The copying and record ink is of too heavy a body to please most writers, or at least they get that notion, so there is a Federal Specification, TT-I-563, Ink; Writing. The specification was written originally to provide ink for use in post-office lobbies, where the conditions are devastating to pens. It is less corrosive to pens than the copying and record ink, and contains only one-half as much iron. For the latter reason, it is not considered suitable for records.

The ink must contain enough dye to give a good color to the fresh writing, so in this ink there must be as much as there is in copying and record ink. It is not recalled when it was decided that the standard ink should contain 3.5 g of dye in 1 liter. At least until 1920 the specification for "Treasury Standard" writing ink called for only 2.2 g of Bavarian blue in that volume. This was the amount used by Schluttig and Neumann. Many commercial writing inks contain considerably more than the 3.5 g of dye now required by the Federal specification for iron gallotannate ink.

Black-black writing ink seems not to be popular, possibly because there is no dye that looks truly black when the usual small amount is added to iron gallotannate ink. Comparatively dilute solutions of the so-called black dyes are blue or purple. It is possible to get around this difficulty by mixing three dyes in the correct proportions. In some tests made by this Bureau, solutions of the same concentration of acid black *N*, brilliant crocein *M*, and orange *G* were mixed in different volumes until the solution was of as dark a gray as could be obtained. More concentrated solutions of the dyes, if mixed in the same proportions, would have yielded a black. To get the darkest gray took 75 ml of the solution of acid black *N*, 15 ml of brilliant crocein *M*, and 10 ml of orange *G*. Because the three solutions were of the same concentration, the dry dyes could have been mixed in the same proportions by weight, and when dissolved the solution would have had the darkest color possible with these particular dyes. Other lots of these dyes might not have the same color strength, and the proportions might have to be changed, but it does not take much time or dye to find out. As little as 0.1 or 0.2 g of dye in 100 ml of water is enough, because the solutions should not be so strong that they cannot be seen through easily in the 100-ml glass-stoppered measuring cylinder, in which it is most convenient to mix them.

For a number of years the standard writing ink was a solution of tannic acid, 11.7 g; gallic acid crystals, 3.8 g; ferrous sulfate crystals, 15.0 g; hydrochloric acid, U. S. P., dilute, 12.5 g; carbolic acid (phenol), 1 g; and soluble blue (C. I. 707; Sch. 539), 3.5 g, in water enough to make 1 liter.

In an amendment to the Federal specification adopted April 1940, the following formula is now used for the standard ink. The materials for making the ink must be of the same quality as for the standard copying and record ink.

*Standard Writing Ink*

	<i>Grams</i>
Gallic acid crystals.....	10.0
Ferrous sulfate crystals.....	15.0
Tartaric acid.....	1.0
Soluble blue (C. I. 707).....	3.5
Water to make a volume of 1 liter.	



This is the same as the formula for ferrous sulfate ink powder, which is discussed in detail in section II, 6 (b). This section should be read carefully by anyone who wishes to make this ink.

The Federal specification provides for the purchase of writing ink as fluid, as concentrated ink, and as powders or tablets.

(1) *Concentrated ink*.—Concentrated ink is acceptable if it meets all the requirements of the specification. 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 an equivalent amount of sulfuric acid, which is nonvolatile, must be used in concentrated ink.

Concentrated ink occupies less space and weighs less than its equivalent in writing ink. The small bottle is not so apt to be broken in shipment as the quart bottle of fluid, to say nothing of the saving in postal or express charges. The concentrated ink is also less apt to freeze and burst the bottles than the more dilute fluid ink; 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. When the Federal specification for writing ink was written and for some years afterwards, the few samples of these forms of ink which had been examined by the National Bureau of Standards consisted wholly of dyes, or else they were quite unsatisfactory mixtures that purported to make iron gallotannate ink. 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 to replace hydrochloric or sulfuric acid. Not until 1931 did the Bureau receive for test a satisfactory iron gallotannate ink powder. Since then the product of one other manufacturer has been found to meet the requirements of the specification. In addition, a chemist of the Bureau developed the two formulas 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 performance on paper, a great number and variety of formulas were systematically studied by one of the chemists of the Bureau. 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 sulfuric acid by less than an equivalent amount 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 in section II, 6 (b).

All three formulas in this section make writing fluids which conform to the requirement of the Federal specification for writing ink that there shall be 3 g of iron in 1 liter. Streaks made with the inks darken not quite as much as those made with the standard ink, but the difference is not so great as to justify the rejection of any of the three.

(1). *Ferric sulfate ink powder*.—The first of the formulas for ink powder is a departure from custom, in that ferric sulfate instead of ferrous sulfate is used in it. The weights of the ingredients needed to make 1 liter of writing ink are:

## Ferric Sulfate Ink Powder

	Grams
Gallic acid crystals.....	10. 0
Ferric sulfate, anhydrous.....	10. 7
Oxalic acid crystals.....	2. 0
Soluble blue.....	3. 5

The weight of ferric sulfate called for, 10.7 g, if strictly anhydrous and pure, would contain 2.99 g of iron, which is near enough to the desired 3 g. Because the salt is never anhydrous, it is best to determine its iron content and from this to calculate the weight of it that will contain 3 g of iron. The salt should contain no free sulfuric acid. Ink made by this formula does not corrode ordinary steel pens excessively, but it forms on them a thin, yellowish coating of ferrous oxalate.

Because gallic acid dissolves slowly in water at the ordinary temperature, it is a good plan to use water as hot as can be put into the bottle without danger of cracking it. This suggestion applies also to the next two formulas.

(2). *Ferrous sulfate ink powder*.—A formula<sup>6</sup> that makes a still better ink powder than the preceding is the one adopted for standard "writing ink," and is given on an earlier page. A discussion of the precautions that must be taken in using it is to be found in section II, 6 (b).

It will be noticed that neither of these formulas for ink powder requires the use of an antiseptic to prevent the growth of molds and other organisms. There has never been any reason to think that an antiseptic is needed, because none of the numerous samples made for experimental work and for actual use has ever become moldy. If anyone who makes ink by either formula thinks some preservative should be used, it is suggested that 1 g of benzoic acid be added to the formula, though this has not been tried by this Bureau.

(3) *Concentrated iron gallate ink*.—The third of the new formulas does not make ink powder, because in it sulfuric acid is used instead of tartaric acid. For this reason it is suitable for concentrated ink. Although not so named in the original published description, it may be called:

## Concentrated Iron Gallate Ink

	Grams
Gallic acid crystals.....	10. 0
Ferrous sulfate crystals.....	15. 00
Sulfuric acid, conc. (95 percent).....	0. 69
Soluble blue.....	3. 5
Water to make a pasty mass or, if for writing fluid directly, enough water to make a total volume of 1 liter.	

The formula as originally published called for 0.654 g of anhydrous sulfuric acid. This is so nearly impossible to obtain and to keep that 0.69 g (0.654/0.95) of the familiar 95-percent acid is substituted here. One milliliter of acid of this concentration weighs 1.84 g. So 0.69 g will be only 0.37 ml. A liter of the standard 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 sulfuric acid. The use of only

<sup>6</sup> This formula is protected against the possibility of a monopoly by U. S. Patent 2,088,006, "Ink," granted to E. W. Zimmerman, July 27, 1937, and by him assigned to the United States Government. Anyone who wishes to use the formula for making ink to sell to the public should apply to the Secretary of Commerce, Commerce Building, Washington, D. C., for a nonexclusive license, for which there is no charge. A license of this kind gives the holder the right to make the ink for sale to anyone, but does not give him an exclusive right. The Secretary of Commerce may issue as many of the licenses as he sees fit. Zimmerman's work on the 3 iron gallate inks was published in J. Research NBS 13, 35-40 (1935) RP807.

0.69 g, or 0.37 ml, of this corrosive acid is greatly to the advantage of the new formula. As when making ferrous sulfate ink powder, the iron content of this salt must be considered.

It is unfortunate that gallic acid is so little soluble that the formulas in this section cannot be modified for making record ink with 6 g of iron in 1 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 it will dissolve still less at lower temperatures. The presence of the iron salt 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.

#### (f) FOUNTAIN-PEN INKS

It seems to be the firm belief of many persons that fountain-pen ink has special properties and virtues not possessed by other kinds, which make it suitable for this purpose. This belief is not in accord with the facts. Any ink that is reasonably free from sediment which may clog the pen, that is sufficiently fluid, and that does not too quickly evaporate and leave a crust on the point, can be used in a fountain pen. Anyone with an open mind can convince himself that it is not essential for the bottle to be labeled "fountain-pen ink." The former writing ink of Federal Specification TT-I-563 was recommended for use in fountain pens. Ink made by the formula for ferrous sulfate ink powder has been used in a fountain pen for 13 months, without the necessity of washing out the reservoir or of doing more than wipe off the point occasionally. Even the heavier-bodied copying and record ink of Federal Specification TT-I-521 works nearly as well as the writing ink.

Occasionally the complaint is made, not that the ink clogs the pen, but that it flows too freely. This is not always the fault of the ink, and the simple remedy is to fill the pen. If the pen is nearly empty, and is cooler than the hand when it is picked up, the ink may flow too freely at first. The reason is that the relatively large bubble of air in the pen, above the ink, expands from the warmth of the hand and forces out a drop or two of the ink. If the pen is nearly full, the bubble is small, and it can not expand enough to force out any ink.

It might be supposed that a very fluid ink would tend to drip from the pen, and that this tendency would be still greater if the ink also had a low surface tension. If a liquid has a low surface tension and is allowed to fall slowly from an orifice, the drops will be smaller than those of a liquid which has a high surface tension, when it falls from the same orifice. The same applies when they are allowed to drip from a point. However, according to Miner and Saylor,<sup>7</sup> the fluidity and surface tension have little to do with the tendency of an ink to flow too freely from a pen. They found no great differences between the fluidities and surface tensions of ordinary writing inks and inks to which an alkali had been added to make them sink rapidly into paper, though the latter had a tendency to drip from the pen. According to Miner and Saylor, ink will flow too freely on account of its "wetting power;" that is, its power to spread in a uniform thin layer on the pen. To overcome the spreading of the alkaline ink which they patented, they added a small proportion, in some cases as little as 0.02 percent, of a substance which seemed to form a film

<sup>7</sup> C. S. Miner and G. H. Saylor, U. S. Patent 1,932,248, Permanent Quick-Drying Writing Fluid (Oct. 24, 1933).



over the metal pen, and thus kept it from being wetted by the ink.

The rate at which a liquid will flow from an orifice can be used to measure its fluidity. In order to get an idea of the relative fluidities of the old standard "writing" and the "copying and record" ink, the time required to empty an 80-ml pipette filled with ink was determined. When the pipette was filled with distilled water, it emptied in 99 seconds. "Writing" ink took 100 seconds to flow from the pipette and, surprisingly, "copying and record" ink was found to take only 101 seconds. It did not seem worth while to prepare some of the old "Treasury Standard" ink, with 10 g of gum arabic in a liter, to find out whether there was any justification of the old complaints that it had "too heavy a body." It is more important to know that the present "copying and record" ink is nearly as fluid as water, and that it can be used in a fountain pen.

One of the worries of those who use fountain pens is the fear that the ink may damage their pens. A solid gold point cannot be rusted by anything that would be in the ink.

A vital part of a fountain pen is the rubber bag which holds the ink. The general use of the self-filling pen, which has almost supplanted the older kind with the medicine dropper, seems to be good evidence that the rubber bags are not damaged by ink. The failure of a bag in an old pen is no proof that the ink is to blame. Rubber does not last indefinitely. It will take up a few hundredths of a percent of water from the ink, and no doubt small amounts of the other ingredients, but probably not enough of all of them together to cause damage. Rubber bands, which are comparable to the grade of rubber of which the ink bags are made, take up almost no soluble blue from a solution of the dye.

## 6. PREPARATION OF IRON GALLOTANNATE AND GALLATE INKS

### (a) IRON GALLOTANNATE INKS

In the formulas already given and in those on the pages which follow, when water is called for it is to be understood that distilled water is best, with rain water the second choice. There are parts of the United States where the water of streams and wells is so "hard," because of the calcium bicarbonate dissolved in it, that a substantial portion of the acid in iron gallotannate and gallate inks will be neutralized if this natural water is used for making them. Water which contains 300 parts per million of calcium, calculated as the carbonate, 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 1 liter of copying and record ink. Because the quantity of free acid is cut to a minimum in the formula, it is evident that the stability of the ink will suffer if so large a part of the acid is neutralized. Writing ink contains less acid than the other, so this hard water will neutralize a larger proportion of the free acid. Water that has been softened by the zeolite, or base-exchange, process is as alkaline as before the treatment, and will neutralize as much of the acid.

To make a liter of standard gallotannate ink, dissolve the gallic and tannic acids in about 600 ml of the water at about 60° 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.<sup>8</sup> Stand the flask on a flat coil of heavy wire or on some other device that will keep it from 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 sulfate, which will quickly dissolve. The contents of the flask should then be allowed to cool to the temperature for which it is calibrated, 20° C (68° F). Meantime dissolve the dye in a separate portion, of about 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 is rinsed, there will be not more than a few solid particles left in it. If the dye leaves a pasty coating on the filter paper, it is not likely to make good ink. When the solution is at the right temperature, the carbolic acid can be added, and then enough water to make the total volume 1 liter. The contents of the flask must then be mixed very thoroughly by inverting the flask a dozen or more times.

Hydrochloric acid is a solution of a gas, the true acid, in water. The usual concentrated acid contains about 36 percent by weight of the gas, and the rest is water. The U. S. Pharmacopoeia 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 it gives directions for preparing it. There are reasons for suspecting that some who make ink by one of the formulas 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 dilute 10 parts by weight of the concentrated acid with 90 parts of water, they will have only 3.6-percent acid. The right 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 densities of the liquids must be taken into account. The density of water at all ordinary temperatures can be taken as equal to 1 g per ml. The density of 36-percent hydrochloric acid is about 1.19 g per ml. Hence 100 ml will weigh 119 g, and will contain 42.8 g of hydrochloric acid gas, the last figure being 36 percent of 119. To prepare 10-percent acid, add 309 ml, or g, of water. This will give a total weight of 428 g, containing 42.8 g of hydrochloric acid gas.

One part by weight of hydrochloric acid gas is chemically equivalent to 1.345 parts of 100-percent sulfuric 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 formula for 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 sulfuric acid; or  $1.77/1.84 = 0.95$  ml.

<sup>8</sup> When a flask stands in a vessel of water, there are spots where it is in actual contact with the heated bottom, because there is no film of water between the 2 surfaces. At these spots the glass may become overheated, and is apt to crack when the bottle is moved, on account of the sudden cooling.

## (b) IRON GALLATE INKS

It was pointed out in the first paragraph in section II, 5 (e) that the two formulas for powder make ink which keeps well in the bottle, provided dye of satisfactory quality is used. Three or four manufacturers who tried the formula for the ferrous sulfate powder said that it made ink which had poor keeping qualities, and this led to the suspicion that perhaps the early deposition of sediment about which they complained was due to the dye. Accordingly, 10 lots of ink were made, by the formula for the ferrous sulfate powder, which differed only in that each contained a different brand of dye. The 10 dyes were from 8 separate sources. During the 2 weeks of the usual sediment test (see section IV, 1), 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 former gallotannate writing ink of the Federal specification. The formation of sediment is due chiefly to the action of oxygen from the air, and if gallotannate ink is kept in a bottle which is only about half filled, it 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 ferrous gallate formula, and containing dye that was satisfactory, was kept in a half-filled bottle for 8 months before any sediment could be seen in it. It seems that the only good way to find out whether a given lot of dye is suitable for making this ink powder is to try it in a small batch of the ink. Anyone who disregards this warning may find that he has thrown his money away by making a lot of worthless ink powder. While the formula was being developed, it happened that the two or three lots of dye that were on hand were of satisfactory quality.

Strange to say, if the ink is made with no dye at all, it is not stable, and becomes cloudy within a week, even in a filled bottle. The reason for this is not known, but the actual fact has been checked a number of times, with materials from different sources. Perhaps the dye molecule acts as an antioxidant and retards the formation of sediment; or it may be 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 fine particles of iron gallate in the solution.

When preparing a supply of the standard ink, it should be borne in mind that even the purest ferrous sulfate may not have the composition shown by the formula,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . When kept in a tightly closed bottle, it retains its pale green color for years, with little or none of the rusty tone that indicates more or less oxidation to basic ferric sulfate. Ferrous sulfate may contain a little free sulfuric acid. A commoner fault is not that it contains objectionable amounts of impurities, but that there is too much iron in it. This is the result of losing part of its water of crystallization when exposed to the air, unless the relative humidity is very high. Evidently if the salt does not contain as much water of crystallization as the formula shows, 15 g of it will contain more than the 3.0135 g or, rounded off, 3 g, of iron assumed in the formula, according to the amount of water of crystallization lost. Even if the ferrous sulfate has just been bought, it must not be taken for granted that it has the right composition, because it may have lost part of its water while it was being dried at

the factory, and before it was put into the packages. An analysis of a sample taken from half-way down in a newly opened bottle of the salt of reagent grade showed that it contained about 3 percent too much  $\text{FeSO}_4$ .

Special tests were made with a freshly prepared sample that was precipitated from solution by adding alcohol, dried quickly by suction in a funnel and then on filter paper, and weighed at once in a shallow dish. Another portion was analyzed before its moisture content could change, and was found to contain 19.96 percent of ferrous iron, instead of the theoretical 20.09 percent calculated from the atomic weights. The corresponding weights of iron in 15 g of the salt are 2.994 and 3.013 g, respectively. Further calculation shows that there was 0.051 g, or 0.34 percent, too much water or alcohol. The sample in the shallow dish was exposed to the air, and was weighed daily for several weeks. On the twelfth day it showed a loss of 20.14 percent. In actual weight this was 31 times the 0.51 g of excess moisture, which clearly shows that there must have been a considerable loss of water of crystallization. The details of the calculation need not be given, but the loss over and above the 0.051 g amounted to 19.49 percent. When  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  loses  $3\text{H}_2\text{O}$ , the percentage loss is 19.44. The loss of 20.14 percent in the first 12 days was practically the maximum—5 weeks later it was only 20.15 percent—because the weight changed with the relative humidity of the air. Two weeks before the value 20.15 was observed, there were two days with a humidity above 80 percent, and the sample then showed a loss of only 17.25 percent.

These details have been given because it is almost impossible to convince people that although the ferrous sulfate may seem to be in perfect condition, it should really not be used for making standard ink, unless it is analyzed and any excess of iron is allowed for. This applies also to the use of the sulfate in formulas in which the amount of free acid is cut to the minimum, as in the formula for ferrous sulfate ink powder. Grinding may cause a great loss of water.

To show how to allow for the loss of water, suppose the sulfate, after thorough mixing and careful sampling, is found to contain 5 percent more iron than the amount calculated from the formula,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . That is, it contains 25.088 instead of 20.088 percent. Then by the proportion

$$25.088:20.088 :: 15:x.$$

we get  $x=12.01$ . This means that 12.01 g of the partly dehydrated sulfate contains as much iron as 15 g of sulfate that has the composition shown by the chemical formula. To prove this, 25.088 percent of 12.01 is 3.0131, and 20.088 percent of 15 is 3.0132.

## 7. ACTION OF HYDROCHLORIC ACID AND SULFURIC ACID IN INK

There can be little doubt that nearly all the blue-black writing ink sold contains sulfuric instead of hydrochloric acid. The lower cost of sulfuric acid and its freedom from the fumes which make hydrochloric acid disagreeable to handle would seem to be sufficient reasons for its general use. In addition, it is said that sulfuric acid makes the better ink. According to one manufacturer, hydrochloric acid causes the formation of a little ferrous chloride, by reaction with the sulfate, and this reducing agent bleaches the dye. Tests made at this Bureau failed to show that a solution of ferrous chloride acidified with hydro-



chloric acid bleached a dilute solution of soluble blue, though the mixture stood in a corked test tube for 8 days. In this test, as well as in those to be described, the solution of dye was weak enough to show slight changes in color when in a test tube held against the light. Any action of a reagent would be proportionately greater on a small amount of dye than on a large amount. The manufacturer also said that ink which contains hydrochloric acid does not noticeably change color until it has been kept for at least 30 days. This suggested that any bleaching of the dye might be due to the oxidizing action of ferric chloride formed by the slow diffusion of air through the cork into the bottle. If the ferric salt did not directly bleach the dye, it might act as an "oxygen carrier," so that the color of the dye would be destroyed. One or two preliminary tests with a solution of ferric chloride acidified with hydrochloric acid seemed to show that it caused slight bleaching. Three series of tests were then made with mixtures containing known quantities of the substances involved.

In the first series, solutions containing the same percentage by weight of soluble blue from three sources were prepared. These solutions were not identical in depth of color nor in tone. Two solutions containing the same percentage of ferrous sulfate were also prepared. One solution was acidified with sulfuric acid and the other with hydrochloric acid. Six mixtures were prepared, each with a measured volume of a dye solution and one of the solutions of ferrous sulfate. The mixtures were kept in Erlenmeyer flasks, closed only by pieces of paper to keep out dust, but not to prevent evaporation nor ready access of air. As controls, to follow any changes in color, some of each solution of dye was kept in a tightly corked bottle. The bottles and flasks were in a dark closet except when they were in use. Beginning May 11, and at intervals until October 25, the color of each mixture and dye solution was tested by letting a small, measured portion flow across an inclined sheet of paper. All the "streaks" of each solution were made on the same sheet of paper. Toward the end of the experiment, the streaks became dingier in color, but the results did not clearly show that one acid was worse than the other, so far as the bleaching of the dye was concerned.

In the second series of experiments, solutions of only two of the samples of soluble blue were used. In each of 5 test tubes, 8 ml of dye solution was mixed with the same volume of a solution of ferric sulfate which contained just enough sulfuric acid to keep it clear, yet not enough to destroy the brown color due to the presence of basic sulfate. To each of the test tubes were then added 4, 3, 2, 1, or 0 ml of distilled water, and, respectively, 0, 1, 2, 3, or 4 ml of dilute sulfuric acid. The mixtures were thus all of the same volume, and their acidities increased by regular steps. Similar mixtures were made with a slightly basic, but clear, solution of ferric chloride and dilute hydrochloric acid. For each dye, two control tubes without an iron salt, one with 4 ml of sulfuric acid and the other with 4 ml of hydrochloric acid, were prepared. The tubes were loosely covered with paper, which kept out dust but did not prevent slow evaporation. Within 24 hours there was sediment in a few of the tubes which contained ferric chloride, and when the experiment was ended 4 weeks later, only the most acid mixture with one of the dyes was clear. There was no sediment in any of the tubes which held the ferric sulfate mixtures. The ferric chloride mixtures were all definitely but not

conspicuously paler than the corresponding control without iron. This was true even of the mixture which stayed clear.

During the 4 weeks of this experiment the level of liquid in the tubes dropped about  $\frac{1}{2}$  inch below the initial depth of 4 inches. In this  $\frac{1}{2}$ -inch space the glass of all 20 tubes which contained a ferric salt was stained with ill-defined horizontal blue rings, but there was hardly a trace of blue stain in the control tubes. With the same ferric salt, one of the dyes caused more staining than the other, and with the same dye, ferric chloride caused more staining than the sulfate. When the liquid was poured off and the tubes were filled with distilled water, the sediment and the blue rings dissolved only partly in the course of about an hour. A little hydrochloric acid added to the water quickly dissolved the sediment, but the blue rings took a long time to go into solution. Some of the sediment was filtered off, washed with water to remove the ferric solution, and then ignited in a porcelain crucible. The ash showed by its color that it contained a large proportion of ferric oxide.

The second series of tests showed that there was no bleaching of the dye by oxidation, and that the ferric chloride, but not the sulfate, caused some of the colloidal particles of dye to flocculate and settle to the bottom of the liquid. Some other observations are in accord with this explanation. When the clear liquid was poured off the sediment into a beaker, the latter was at once covered with a blue stain which was not removed by water, unless aided by rubbing. The same clear liquid stained filter paper, asbestos, bentonite (an extremely colloidal clay-like mineral), titanium dioxide, and barium sulfate, and the stained materials did not recover their whiteness when they were soaked overnight in a large volume of distilled water.

For the third series of experiments, four inks were prepared by the former formula for the gallotannate "writing" ink of the Federal specification, except that only 1.5 g of dye per liter, instead of 3.5 g, was used. With each of the two dyes of the second series two inks were made, one with hydrochloric acid as required by the specification, and the other with an equivalent quantity of sulfuric acid. The four inks were kept in corked bottles, which were only half-filled. From time to time, 1 ml of each was diluted with 10 ml of distilled water, and the depth of color compared. After 2 months there was no difference in color to show that hydrochloric acid had a harmful effect upon the ink. Perhaps, in spite of the large amount of air in the bottles, the inks suffered too little oxidation to contain enough ferric chloride to precipitate any dye. If oxidation can be prevented, no ferric chloride will be formed, and the amount of free hydrochloric acid will not diminish.<sup>9</sup> A sample of about 200 ml of standard writing ink was hermetically sealed in a bulb by melting the glass together. After being kept for 13 years, it showed only traces of sediment. According to Hinrichsen and Kedesdy,<sup>10</sup> the sediment which forms in ink from which air is excluded contains almost no iron, but consists of condensation products of the gallic and tannic acids. The sediment formed by oxidation contains an abundance of iron.

Ink is sold in bottles, and these should be nearly full. The corks should be as perfect as possible, and not the inferior ones with numer-

<sup>9</sup> The equation shows how the amount of free acid diminishes when ferrous iron is oxidized to ferric:



<sup>10</sup> Mitt. Materialprüfungsamt 25, 317 (1907).

ous cavities, which make it easy for air to get to the ink. It is said to be best to keep the bottles in the dark.

Anyone who has the ingredients at hand and the necessary facilities can quickly prepare blue-black ink. The average person, not so equipped, would find it a nuisance to make a fresh supply of ink every few months. If he made a supply large enough to last 2 years, say, he might have to throw most of it away, because it would be too full of sediment. It seems wiser to buy one of the numerous brands of good writing ink that can be obtained almost everywhere. A 4-oz. bottle of ink will do a vast amount of writing, and there is no economy in buying a quart of it because it is sold at a lower rate per fluid ounce, if it becomes an annoyance to use.

### 8. DIAMMONIUM HYDROXYFERRIGALLATE INK

An ink which is of no present commercial importance, yet which gained some prominence in the newspapers on account of its having been found to have so little harmful action on paper in an accelerated-aging test (see section II, 13), is a solution of diammonium hydroxyferrigallate.<sup>11</sup> In 1908 two Rumanian chemists<sup>12</sup> published the results of their studies on iron-gall inks, and among other things described the method for preparing this compound. They said that a 7- to 8-percent solution of it in water made good writing ink.

For those who may be interested, the method as taken from the abstract in the *Chemisches Zentralblatt* is given here. Dissolve 7.5 g of ferric chloride (presumably  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 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 diammonium hydroxyferrigallate, which is filtered off and washed, first with dilute alcohol and then with strong alcohol. The 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, in the absence of definite instructions by the authors, 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 strong alcohol and 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. The solution soon becomes turbid and deposits sediment in the bottle.

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 that is needed increases the cost. A few experiments made at the Bureau indicated the possibility of preparing

<sup>11</sup> In the preceding edition, C413, of this Circular, this compound was called "ammonium ammoniumoxyferrigallate," which was the name used in the third edition of "Inks, Their Composition, and Manufacture" (see footnote 1). In the fourth edition of his book, Mitchell calls the compound by the more satisfactory name at the head of this section.

<sup>12</sup> 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, in a footnote on page 100 of the fourth edition of his book, refers to Zetsche's criticism of the work of Silbermann and Ozorovitz, but gives the wrong volume and year of the journal in which the criticism appeared. The correct citation is *Liebigs Ann. Chem.* 435, 233 (1924).



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 difficult task.

#### 9. FREEZING OF INKS

There seems to be a general belief that freezing precipitates the coloring matter and makes inks pale and watery. There is much colloidal matter in inks, and it did not seem impossible that freezing would cause this to flocculate, or collect in large particles that would settle to the bottom of the liquid. If this should happen, the precipitated matter might not redisperse when the ink became warm again. In order to find out just what would happen when they froze, five inks were prepared. Two were prepared by the formulas for "copying and record" and the former "writing" ink. Iron gallate ink was made by the formula for "ferrous sulfate ink powder." The red ink was the standard of the Federal specification, made by dissolving 5.5 g of brilliant crocein M in 1 liter of water. The fifth ink was a water solution containing 15 g of soluble prussian blue in a volume of 1 liter. It quickly formed a clear solution in distilled water, without the customary addition of oxalic acid. A similar solution, after being kept at room temperature for 7 years, contained only traces of sediment.

Portions, of 100 ml each, of these inks were put into the tall, narrow, 4-oz (120 ml) bottles commonly used for samples of lubricating oils. The tightly corked bottles were kept overnight in a refrigerator maintained at  $-18^{\circ}\text{C}$  ( $-0.4^{\circ}\text{F}$ ), at which temperature all the inks froze solid. On thawing, there was a little of a whitish deposit, probably gallic acid, in the two iron gallotannate inks. It dissolved at room temperature when the bottles were shaken a few times. Before the red ink froze, but when it was well chilled, some of the dye separated from solution and settled to the bottom. This dye redissolved when the ink warmed to room temperature, though the bottle was not shaken. As could have been predicted, the iron gallate ink deposited a rather large amount of its gallic acid but, on repeated shaking at room temperature, it all went into solution again. The three iron inks and the red ink were frozen and thawed three times over a period of several days, and always with the same results. None of the bottles were broken by the freezing.

The solution of prussian blue was frozen twice. At each freezing a part of the blue separated in a layer about 2 millimeters (mm) thick at the surface, and the rest of it formed a large irregular mass extending down one side and over the bottom of the bottle. At each freezing the prussian blue separated so completely from the water that the mass of ice looked nearly colorless. It was faintly blue, possibly because some of the prussian blue stained the glass. When the ice melted, all the blue soon went into solution. The curious behavior of the prussian blue led to one more experiment. Oxalic acid, at the rate of 5 g in a liter, was added to the solution of prussian blue. When this solution was frozen there was no separation of coloring matter.

The Bureau has not made any measurements of the freezing points of inks, but it can be said that they will be lower than the freezing point of pure water. It is a general principle that the solution of any



solid in water freezes at a lower temperature than does pure water, and the more concentrated the solution, the lower its freezing point. Iron gallotannate inks will freeze at lower temperatures than dye inks, because the iron inks contain more dissolved material than is in the usual dye ink. Many dyes form colloidal solutions, which will freeze at practically the same temperature as pure water, unless the dye contains the usual admixture of sodium chloride or other soluble salt.

#### 10. 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 that the ink contains a black instead of a blue dye. In a few hours the writing becomes perceptibly darker because the ferrous gallotannate, which is not strongly colored, has 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 is pronounced in a comparatively few minutes, and appears to be complete in a day or two. The oxidation that causes the blackening does not cease abruptly when the ferrous iron is all 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, and if this occurs before the gallic and tannic 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. In the further course of time the writing will become brownish black, then dark brown and, if the paper lasts 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 about some of the factors that influence the rate at which ink ages on paper. The first factor is 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 cannot 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 contained too small a proportion of gallic and tannic acid for the amount of iron, the writing may become rusty in a comparatively few years.

The fluidity of the ink and the absorptiveness of the paper, the kind of pen point, and the heaviness of the hand of the writer influence the quantity of ink in the written characters and thus play their part in the aging. If the writing is blotted, instead of being allowed to dry naturally, the ink is handicapped at the start, yet those who use a blotter to keep what they write from becoming accidentally smeared can hardly be blamed. In explaining the desirability of a quick-drying writing ink, a United States patent<sup>13</sup> says:

Inks hitherto available for writing purposes require appreciable time for drying, which necessitates frequent blotting and constant care. This is always

<sup>13</sup> George B. Ottley, U. S. Patent 1,897,071, Quick-Drying Ink (Feb. 14, 1933).

an annoyance; and in special cases is even a nuisance, as in the case of left-handed people who have a tendency to drag the hand across the freshly written characters. In other cases, as in bookkeeping or in making signatures, the necessity of applying a blotter makes many useless motions, and in the aggregate wastes a considerable amount of time. These and other objections show that it is desirable to have a quick-drying ink which can be covered almost immediately without blotting; but none has been known, so far as I am aware.

It will be seen that the patentee overlooked a strong argument in favor of his ink, because if none of it is removed by a blotter, the writing will be more permanent. An inspection of old notebooks, ledgers, and similar records is apt to disclose great differences in the appearance of writing of the same date and in the same hand. These differences must be partly due to the use of a blotter on some of the writing.

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. Dampness may permit the growth of molds, which destroy both ink and paper.<sup>14</sup> 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 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.

Earlier in this section it is said that fresh writing soon becomes black when the acid in the ink is neutralized by exposing it to the fumes of ammonia. Paper that contains calcium carbonate, which reacts strongly alkaline to some indicators, as well as other alkaline paper, has the same effect upon the writing as the fumes of ammonia. Streaks were made by letting small portions of blue-black ink flow across paper containing calcium carbonate, paper coated with clay and an alkaline binder, and two nonalkaline writing papers. In order to detect changes in color more easily, the ink was diluted with distilled water, in most cases to four and eight times its original volume. The streaks on the two writing papers were light blue, but those on the two alkaline papers became dark in a few seconds. At the lower ends of the streaks, where the excess dripped from the edge of the paper, there were clots of the black ferric compound.

It is practically certain that the rapid blackening of the streaks on the alkaline papers is related to the familiar phenomenon of the rapid oxidation of ferrous hydroxide when it is precipitated by the addition of an alkali to a solution of ferrous sulfate. If the sulfate contains no trace of ferric iron, the hydroxide is at first white, but in contact with the air it quickly turns to a muddy green, and then to the rusty color of ferric hydroxide. On the other hand, an acidified solution of ferrous sulfate oxidizes rather slowly.

It is believed that the rapid change in the color of the ink on the alkaline clay-coated paper is not caused in any way by adsorption of part of the ink. The clay-like mineral, bentonite, is highly adsorptive when wet. Sheets of the two kinds of paper that did not cause the darkening of the streaks of ink were coated on one half by brushing

<sup>14</sup> C. A. Mitchell and D. R. Wood, *Action of molds on ink in writing*, Analyst **63**, 111 (1938).

over them a thin paste of bentonite in a solution of dextrin as a binder. When the paper was dry, streaks of diluted ink were made on the coated and uncoated halves of the sheets. There was no sign of blackening, but the streaks on the bentonite were deeply colored, on account of the adsorption of the ink.

### 11. DATING A DOCUMENT

Examiners of documents base their conclusions as to the age of writing to a considerable extent on its appearance. As was 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 a week, more or less. The writing continues to be acted upon by the oxygen of the air, so that at 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 upon a number of factors, as was explained in the preceding section.

When 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 characters. If it was an iron ink, the presence of blue dye is tested for. The ease with which certain reagents dissolve the dried and oxidized 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 document or sample of writing. However, the Bureau was practically forced to examine a number of samples of writing in order to get some definite information about the length of time it takes for the blue dye to disappear. In connection with a case in court,<sup>15</sup> 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 that all three were written with 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 is commonly said, though some 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 in discussing the results of tests made on a number of bank checks of different ages. He says:<sup>16</sup> "In abnormal cases, where an excessive amount of ink has 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 of the National

<sup>15</sup> H. Manchester, *The Black Tom Case*, Harpers Mag. No. 1075, 60-63 (December 1939).

<sup>16</sup> See p. 211 of the book cited in footnote 1.



Bureau of Standards, in university lecture notes, and in legal papers.<sup>17</sup> The samples of writing were dated from 1851 to 1918. The tests were made in 1933, so all the writing was 15 or more years old. It cannot 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 deep black to a pale color, care was taken to test a medium-dark character as well as an intensely black one on each page. So, in half of the tests the writing contained only a moderate 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 first 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 fingertip, 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 2 tests made on writing dated 1881, 1 showed dye faintly and 1 distinctly. Two tests of writing of 1879 were negative, while 1 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. If the testing had been limited to writing that was just 15 years old—1918—what the 2 experts said would have been upheld, because 4 samples of that year failed to show any sign of dye. Yet older 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, 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<sup>18</sup> in examining their bank checks differed from that of this Bureau. 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 treatment with distilled water alone, 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

<sup>17</sup> What follows in this and the succeeding 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).

<sup>18</sup> See p. 182 of the 3d edition of the book cited in footnote 1. The procedure is also described on page 210 of the present, or 4th edition, which had not been published when the Bureau's tests were made.

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 2 places, and the 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 6 tests, while for 1896, 4 out of 8 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, one should be cautious in 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. 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.

A few years ago a new method for ascertaining the age of writing received considerable notice in technical and other journals. This is the so-called "chloride test," which is based upon the assumption that nearly all writing ink contains hydrochloric acid or metal chlorides. The chlorides spread gradually from the ink marks, presumably 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 character of the paper, and the humidity of the air, which affects the film of moisture. In making the test,<sup>19</sup> 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 hydro-sulfite. 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,<sup>20</sup> the chloride test is unreliable. The paper in which their work is described ends with a list of experts and 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."

In later work Finn and Cornish<sup>21</sup> found that the rate at which chloride migrates in the paper depends upon the amount in the ink and, naturally, upon the atmospheric humidity. Two exceptions to

<sup>19</sup> O. Mezger, H. Rall, and W. Heess, *Z. angew. Chem.* **44**, 645 (1931). See also a historical review and systematic guide for judging the age of writing, by W. Heess, *Arch. Kriminol.* **101**, 7-37 (1937).

<sup>20</sup> R. E. Cornish, J. Finn, Jr., and W. McLaughlin, *Age of inks by the chloride test*, *Ind. Eng. Chem., News Ed.* **12**, 315 (1934).

<sup>21</sup> J. Finn, Jr., and R. E. Cornish, *Ind. Eng. Chem., Anal. Ed.* **10**, 524 (1938).

this were found. Hydrochloric acid, because of its volatility, does not spread in a zone around the writing, but escapes into the air. Stannous chloride, probably because of its oxidation to insoluble basic stannic chloride, also does not spread. The authors end as follows: "Since so many factors are concerned in the chloride test for age of inks, any conclusions regarding the age of writing, as determined by this test, should be viewed with extreme suspicion. Inks used in Federal offices and banks should contain a definitely known amount of sodium chloride. This would not only aid in readily identifying the ink, but would also make it possible to determine something of the time element." The remark about the time element must mean that if two samples of writing done some time apart with the same ink are on a given sheet of paper, the older sample will have the wider zone of chloride around it. This would not be true if both samples of writing were so old that there was no further spreading of chloride around either of them.

In their article, Mezger, Rall, and Heess also discuss the spreading of sulfates from the strokes of the writing into the paper, and suggest this as another means for determining the age of writing.<sup>22</sup>

In a later paper, Finn and Cornish<sup>23</sup> describe a new procedure for showing how far chlorides and sulfates have migrated in the paper from the strokes of the pen. The writing is immersed in a freshly prepared solution containing 1 percent of silver nitrate and 2 percent of lead acetate, in a photographic tray. It is then washed 5 times with distilled water, and treated with a 3-percent solution of ammonium dichromate that has been neutralized with ammonia. This is nearly equivalent to a 3.6-percent solution of ammonium chromate. There must be no excess of ammonia because it will dissolve silver chloride and chromate. In the first solution any chlorides are converted into silver chloride, and soluble sulfates into lead sulfate. These two salts are so slightly soluble that they remain in the paper during the washings. In the chromate bath one is changed into lead chromate, or chrome yellow, and the other into silver chromate which, according to its amount, stains the paper red or pink. According to the nature of the ink, the paper may now show green, light green, blue, black, red, pink, and orange. Final treatment of the writing with a photographic developer ("D72") gives the writing a red to pink color, according to the amount of chloride. The authors conclude with the cautious statement that "if shown that the same ink is used an opinion might be rendered as to the probable date of the inks." To this must be added that the paper must be the same, and kept under the same conditions.

An account of some tests made with a bleaching agent, hydrogen peroxide, on 7 samples of writing, 1 day, 6 months, and 1, 2, 6, 14, and 22 years old, was found in an unexpected place.<sup>24</sup> 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:

1. The inks must be those known as ordinary writing inks, prepared from iron and chromium salts and galls.

<sup>22</sup> See also W. Heess, *Arch. Kriminol.* 26, 13-17 (1935); *Analyst* 60, 338 (1935).

<sup>23</sup> J. Finn and R. E. Cornish, *Differentiation of inks and their chloride and sulfate migrations*, *Ind. Eng. Chem., Anal. Ed.* 18, 174 (1946).

<sup>24</sup> *Workshop Receipts*, 5, 88 (Spon & Chamberlain, New York, N. Y., 1903). The article, *Ink*, is signed by R. Irvine.



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 it. It must be evident to the reader that 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 heavy.

Mitchell<sup>25</sup> makes a similar confession of the limitations of his method for determining the relative ages of samples of writing by their behavior towards a solution of oxalic acid. The bank checks alluded to were tested in order to get an idea of the age of some writing in a will which was in dispute. He says: "In drawing conclusions from such tests care must be taken that the amount of ink, as shown by the microscope, is about the same as that upon the document in question. That is to say, heavy writing must be compared with heavy writing, and the ink must naturally be of the same type."

Another recent contribution to the study of the age of writing is by Rhodes,<sup>26</sup> who studied the rate at which the ferrous iron in writing oxidizes to ferric iron. His reagent was a 1-percent solution of  $\alpha$ ,  $\alpha'$ -dipyridyl in 0.5 *N* hydrochloric acid. With ferrous iron it forms a pink or red compound, but gives no color reaction with ferric iron. By testing from day to day samples of writing done with several inks, he found that at the end of 20 days there was no further oxidation of ferrous iron. With one type of commercial French ink the oxidation was at an end in 15 days. On the other hand, if indigo had been used as the blue dye, the oxidation seemed to be delayed indefinitely. Logwood prevents the determination of iron, because its color masks that of the dipyridyl compound. Fortunately for the test, the presence of the usual kind of blue dye does not interfere. Substances in solution do not all spread to the same extent in paper, but separate more or less completely into zones surrounding the spot where the liquid was put. In the case of ink, the blue dye and the pink iron-dipyridyl compound come to rest in separate zones. By making a series of standard spots with different known amounts of ferrous iron, Rhodes made his test quantitative, and determined the amount left in the writing from day to day. Knowing this, he said it is possible to distinguish between samples of writing, provided they are not more than 30 days old.

## 12. 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 which is only a solution of a dye. When a dye ink fades, it

<sup>25</sup> Page 211 of the book cited in footnote 1.

<sup>26</sup> H. T. F. Rhodes, *The oxidation of ferrous iron in iron gall ink*, Chemistry and Industry 53, 143-145 (1940).



sometimes leaves literally nothing behind on the paper, and if traces of oxidation products remain, they cannot be detected readily, if at all. When an iron ink fades it leaves small quantities of iron oxide in the strokes of the letters, and this makes it possible to restore the legibility of the writing.

The vapors of ammonium sulfide will change the ferric oxide into ferrous sulfide, mixed with "molecular" sulfur. The ferrous sulfide 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 sulfide is oxidized to sulfate in a short time, and there may be bad aftereffects upon the paper.

A 2- or 3-percent solution of tannic acid, or a saturated (about 1.25-percent) solution of gallic acid will also blacken the ferric oxide. This is by far the best treatment, because one of the black compounds of the original writing is again formed, and because neither a strong acid nor a metal salt other than the one desired is left in the paper. In addition, it has been found (see section II, 13) that neither tannic nor gallic acid causes deterioration of paper, in an accelerated aging test. According to Mitchell, this use of tannic acid was recommended by Canneparius in 1660.

Again, a solution of potassium ferrocyanide ("yellow prussiate") slightly acidified with hydrochloric acid will change the ferric oxide into prussian blue. This is a very permanent color, but the salts left in the paper may later cause trouble, either by weakening it, or by staining it blue all over. The method was first used in 1787, in order to find out whether some old documents had been written with a carbon ink or an iron ink. Blagden, who used it, apparently had no thought of the aftereffects. In 1939 Lowy and Campbell were granted a patent for a treatment for preventing the staining of the paper, though they said nothing about preventing any weakening of the paper by salts left in it.<sup>27</sup>

The solution of tannic or gallic acid or of ferrocyanide can be applied with a soft 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 strong 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 are not selective in their action, and thus the writing is restored as dark lines upon a less dark and unevenly colored background. If the entire sheet of paper is treated with gallic or tannic acid, it will become further stained in the course of time, because these acids darken by oxidation. If possible, the excess acid should be washed out by immersing the treated paper in pure water for a short time, and then drying it. This brings up a third method, suggested by an Army officer on whose commission the signature of the President had faded. Enough iron oxide was left behind to enable him to trace over the signature with a pen dipped into a solution of gallic acid. He enthusiastically reported his success in restoring the signature.

<sup>27</sup> Blagden, *Trans. Roy. Soc. (London)* [2] 77, 451 (1787).

A Lowy and C. H. Campbell, *Method of Restoring Inked Documents*, U. S. Patent 2,182,672 (December 5, 1939).

Years ago, when it was decided to place the Declaration of Independence on exhibition in the Library of Congress, this Bureau 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 on the document, it was decided that it would be best not to tamper with it, at the risk of ruining it forever.

This Bureau once solved in an unusual way the problem of deciphering some records that had been charred by fire in an office safe.<sup>28</sup> The papers were separated from one another as well as could be, and each was put between two fast photographic plates, with the emulsion in contact with the charred paper. After a week or two the plates were developed, and legible negatives of the writing were obtained. The gases slowly diffusing from the charred paper fogged the photographic emulsion, except where the residue left by the ink hindered their escape.

An ingenious way to separate the charred pages of a book with a minimum of handling has been described.<sup>29</sup> The pages adhered to one another in a brittle mass. The back of the book was cut off, and the block of pages was saturated with water. While still wet, it was held at the mouth of a furnace, whereupon the steam separated the pages from one another. The writing could then be read as dull black marks on a glossy black background.

### 13. EFFECT OF WRITING INK UPON PAPER

As was said on an earlier page, the condition of old manuscripts 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 sulfuric acid in the ink. It is well established that this acid makes paper brittle. The excess acid may have come from carelessly made ferrous sulfate. Another explanation of the destruction of the paper is that it has been brought about by iron oxide from 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 this Bureau. In addition, solutions of gallic, tannic, and hydrochloric acids and of ferrous sulfate, in various combinations, but of 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 each half of the sheet 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. The loss in folding endurance gives the best evidence of weakening of the paper.

<sup>28</sup> R. Davis, BS Sci. Pap. 18, 445-450 (1922-23) S454.

<sup>29</sup> Workshop Receipts 2, 392. (Spon & Chamberlain, New York, N. Y., 1903.)

The details of the investigation must be obtained from the original article.<sup>30</sup> It will suffice to say here that all the inks which were tested increased the amount of weakening of the paper in the accelerated aging test. The least harmful ink was a solution of diammonium hydroxyferrigallate in water. In the aging test one of the papers without ink retained 72 percent of its initial folding endurance. The same paper, with lines drawn with this ink, retained 68 percent of its folding endurance. This difference is practically negligible. The next best ink caused a drop to 58 percent of the initial folding endurance. This second ink was made by dissolving 15 g. of dialyzed prussian blue, without the customary 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 have caused greater deterioration of the paper. Solutions of gallic acid and tannic acid, alone or mixed with hydrochloric acid, had no harmful effect upon the paper. Ferrous sulfate, either by itself or mixed with the acids, caused decided 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 sulfuric acid, because it has long been established that it is extremely harmful to paper.

If the standard copying and record ink of Federal Specification TT-I-521 is made with sulfuric acid instead of hydrochloric acid, a liter of it will contain 3.54 g of concentrated (95-percent) sulfuric acid. A liter of ink will write many thousands of words, and it might seem as if the small amount of sulfuric acid added to a page of paper by covering it with writing would not cause a detectable increase in the rate of deterioration of the paper. It is not safe to draw such a conclusion, because work done by this Bureau<sup>31</sup> and in other laboratories has proved that a very small amount of sulfur dioxide in the air may cause serious damage to books and documents in libraries. The sulfur dioxide is absorbed by the moisture which paper always contains. The sulfurous acid thus formed is soon oxidized to sulfuric acid, which is not volatile except at a temperature far above that at which paper is charred. Unless it is soon neutralized by some basic substance, it will damage the paper.

#### 14. INK ERADICATORS

When writing is removed with an eraser made of steel or of rubber containing an abrasive substance, the surface of the paper suffers, and it is not easy to write again over the same spot. To avoid this, various chemical solutions that dissolve blue-black ink from paper have been devised as ink eradicators. Whether they will also dissolve dye inks, which are taken up in a later section, depends upon the chemical nature of both dye and eradicator. If the eradicator 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 is their effect upon paper. At first no harm appears, but some of the chemicals will always

<sup>30</sup> 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) RP 779. A summary of this work is given by B. W. Scribner and A. E. Kimberly on page 25 of the Bureau's Miscellaneous Publication M154, Summary Report of National Bureau of Standards Research on Preservation of Records. Both publications give numerous literature references.

<sup>31</sup> Summarized on pages 7 to 14 of the Bureau's Miscellaneous Publication M154, Summary Report of National Bureau of Standards Research on Preservation of Records.



be left in the paper and will finally injure it. As a rule, a brownish spot appears where the eradicator was applied, and after a time 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 apply 1 or 2 drops of pure water. After a few moments remove the water with a blotter, and repeat the operation once or twice. This will not remove all traces of 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. The first two have a bleaching action, which is made more rapid by the acid. 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 instead of javelle water, it should be diluted with water to the same volume of liquid as if it were converted into javelle water. For the acid, 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 36-percent acid. One volume of this with six volumes of water will yield acid which is near enough to the desired 5-percent strength.

Oxalic acid, a poisonous crystalline substance, will dissolve dried and oxidized iron gallotannate ink. For use as an eradicator it should be dissolved in about 20 times its weight of water. Much safer, because it is not poisonous, 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, the United States Department of Agriculture tells how to remove the inevitable ink spots from clothing and other fabrics.

### III. OTHER KINDS OF INK

#### 1. INKS CONTAINING OTHER METALS THAN IRON

It is fair to ask whether it is not possible to make inks with other metals than iron. In the section on indelible marking ink for fabrics there are formulas for a silver ink and for two in which copper sulfate is a necessary ingredient. The first ink leaves on the fabric a black deposit which is essentially silver. In the other two formulas, the copper sulfate acts as a catalyst, to promote the oxidation of the aniline hydrochloride to insoluble aniline black. The copper does not remain in the fabric and give permanence to the marks, but is easily washed out. However, copper sulfate or acetate is sometimes included in formulas for iron gallotannate inks.<sup>32</sup>

At one time it was thought that vanadium gallotannate ink was more permanent than the corresponding iron ink. The noted chemist Berzelius discovered the ink and discussed it in his book, published in 1835. What he said about its permanence was accepted without

<sup>32</sup> Many of the older formulas seen in books call for "copperas," a name still in commercial use for the technical, or less pure, grade of ferrous sulfate. It contains no copper, unless as an impurity. Another old name for it is "green vitriol." Copper sulfate is called "blue vitriol" or "bluestone."



question for many years. As late as 1892, Lehner<sup>33</sup> said, "Vanadium inks cannot be destroyed by any known agents, the writing always remaining plainly legible; and, hence, it would decidedly be the best safety ink if the ammonium vanadate required for its preparation could be more readily obtained in commerce." Yet another noted chemist, Wöhler, who died in 1882, had seen the letters of Berzelius, and had said that they were quite unreadable. It apparently did not occur to Wöhler to treat the faded writing with a solution of gallic or tannic acid. This would have blackened the pale lines of vanadium oxide on the paper and restored the legibility of the writing.<sup>34</sup>

During the first 3 or 4 years of testing inks at this Bureau, among the samples submitted with bids for supplying "Treasury Standard" writing ink there was almost always a logwood-alum ink. The purple-brown of the fresh writing soon changed to a dark red-brown. The bidder in each case was either ignorant of the composition of the ink, or he decided to take the chance that his sample would not be analyzed, and that it might be accepted because of its low price. At any rate, instead of containing 6 g of iron in a liter, the ash of the ink was snow-white, not rusty brown, and contained only a trace of iron. Formulas for logwood-iron and logwood-chromium inks, which have a good black color, are easy to find in books. They offer no advantage over iron gallotannate inks, and it is not necessary to give any of the formulas here.

## 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 discussed briefly, is not a solution of carbon, but a suspension of it in water containing gum or glue. The suspension is not permanent, but to those who write with a brush, instead of with a pen, it makes little difference if the ink must 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 in suspension almost indefinitely. Reference is again made to Mitchell's book,<sup>35</sup> in which the manufacture of India ink by the Chinese is described and illustrated. Lehner<sup>36</sup> gives directions for purifying lampblack for making carbon ink. His method is designed primarily for removing the traces of oil which makes it difficult to wet the lampblack and to disperse it in liquids.

If some carbon black is stirred with water, and is then left to itself, after a time it will settle and leave clear water above. If the carbon is ground with water a long time and the mixture is left 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, the carbon will stay in suspension a long time if it is thoroughly

<sup>33</sup> S. Lehner, *Manufacture of Inks*, translated, with additions, by W. T. Brannt. (H. C. Baird & Co., Philadelphia, Pa., 1892). (See page 101.)

<sup>34</sup> Vanadium inks are taken up by Mitchell on page 146 of his book. (See footnote 1. See also J. Zernike, *Analyst* 62, 457 (1937).)

<sup>35</sup> See footnote 1.

<sup>36</sup> See pp. 147-148 of the book cited in footnote 33.

ground. 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, because the individual particles are so small. Microscopical examination shows that ordinary carbon black consists of clusters of extremely small particles. Grinding does not make these particles smaller, but separates them from one another.

Black drawing ink is a practically permanent suspension of carbon. According to one manufacturer, his ink is ground for 3 or 4 weeks in a ball mill and is allowed to settle for some days before the upper four-fifths is drawn off and bottled. If this is necessary, it is a sufficient reason why carbon ink cannot be made by hand grinding.

Of late years some of the producers have been selling carbon black which needs no grinding, but only vigorous agitation, to make it form a permanent suspension in solutions of appropriate reagents. A correspondent of this Bureau, who sells various inks made in his home, told about his success with black waterproof drawing ink. It is made by mixing one of the special grades of carbon black with a solution of shellac and borax in water, according to the formula provided by the dealer. For a day or two the mixture is stirred occasionally and is then bottled for sale. Users of drawing inks are not apt to look with favor on brands with unfamiliar labels, and it speaks well for the producer of the carbon black that drawing ink which is so easily made satisfies the purchasers. In the absence of definite information about the process of preparing this special carbon, it is permissible to suspect that some of the "wetting agents," that are finding such various uses, play a part.

Water that is clouded by extremely fine particles of clay in suspension will clear quickly if 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 and the borax used to dissolve the shellac which waterproofs it are mild alkalies. When black drawing ink becomes thickened in the bottle, by evaporation of part of the water, it can be thinned with distilled water to which a little pure ammonia water has been added. Too much ammonia will make the ink too alkaline, and it will be apt to "feather," or spread, in paper. It is sufficient if the water has only a faint odor of ammonia. "Household" ammonia should not be used for this purpose, because it is not a solution of ammonia gas in pure water, but contains other substances in solution. Because of their sensitiveness to acids, carbon inks cannot be mixed with iron gallotannate ink, and a fountain pen that has held the latter must be cleaned with great care before filling it with a carbon ink. Carbon inks might be popular, and deservedly so, if it were not so easy to ruin them by ignorance of their peculiarities, or by carelessness.

A strong point in favor of carbon writing inks, of which there are a few brands on the market, is that they are unlikely to contain any substance which will damage paper in the course of time. This is not true of iron gallotannate inks. A surprising feature of carbon writing inks is the resistance of the writing to soaking in water. Lines were drawn on two kinds of paper with a commercial writing ink. One of

the papers was sized with rosin, and the other was in addition surface-sized with starch. This is the bond paper used by the Government Departments for letters. The ink was dried overnight, and pieces cut from the sheets of paper were soaked for 2 hours, either in distilled water or in a solution of white floating soap. This solution was strong enough to make suds. As soon as the pieces of paper were immersed, a cloud of carbon could be seen near the lines, and there was a slight staining of the paper. Yet after being soaked for 2 hours and then dried, the lines were hardly any paler than those which had not been soaked. The soap solution removed but little more carbon than was washed out by pure water. A similar experiment was performed with two waterproof drawing inks from different manufacturers. The lines resisted soaking in distilled water almost as well as the lines of writing ink, but in the soap solution they suffered badly, especially the lines drawn on the bond paper. Drawing ink contains shellac, and this seems to keep most of the ink on the surface of the paper, instead of letting it penetrate. The starch sizing on the bond paper is an additional barrier against the penetration of the ink. Because the lines of the drawing inks were almost entirely on the surface of the paper, they were easily washed off by the alkaline solution of soap. Only the comparatively small amount of carbon that sank into the bond paper was left. The other kind of paper was less effectively sized, more of the ink sank into it, and less of the ink was removed by the solution of soap.

#### (b) PRINTING, CANCELING, AND OTHER CARBON INKS

Black drawing ink contains a comparatively small percentage by weight of carbon and other solid matter, and it does not differ greatly from clear writing 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.

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 cannot give equally good results in printing from ordinary type, a halftone cut, and an engraved plate, to say nothing of other kinds of printing. The paper introduces another important factor in the finished work.

Mimeograph and other duplicating-machine inks require great care in their formulation and manufacture. If the 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 freely. Again, the ink may go through the stencil too easily, and may become smeared over the back of the stencil, and from that to the paper.

The carbon in a canceling ink should be carried into the paper, and remain there in spite of attempts to remove it without at the same time destroying the possibility of fraudulently using the postage stamps a second time. The post offices throughout the country use large quantities of canceling ink. Most of the canceling is done with metal stamps, operated by hand or on canceling machines, but rubber hand stamps are used for canceling on special packages. Two kinds of ink are needed. They are bought on specification, and must meet



the requirements as to composition and consistency. Nothing would be gained by giving the formulas here, but it can be said that they must contain a certain proportion of black dye, reinforced by carbon black.

Formulas for various kinds of carbon inks can be found in books, but they are to 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 different forms of carbon employed as pigments are unlike in physical properties, and they cannot be used interchangeably. The same can be said of the innumerable white and colored pigments of which inks are made. It is possible to measure some of the properties of the pigments and other ingredients of the inks, but this does not tell exactly what the finished inks will be like. The consistency, for example, depends to a great degree upon what is called the oil absorption of the pigment. This differs according to the chemical composition of the pigment, and is closely tied up with its fineness and degree of dispersion.

Federal specifications have not been written for printing, mimeograph, and other inks containing pigments, except drawing inks, because there are no laboratory tests that can be depended upon to show whether the inks will work well or poorly. The only dependable way to test these inks is by practical trial. The Federal specifications for black waterproof drawing ink and for colored waterproof inks which are made with pigments, instead of being clear solutions of dyes, do not have formulas for standard inks with which samples are to be compared.

The difficulties involved in the production of a carbon ink are illustrated in the description of the process by which the United States Government Printing Office makes mimeograph ink.<sup>37</sup>

### 3. DYE INKS FOR WRITING

As was 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. If small amounts of other products remain in the paper, there is no dependable way to convert them into colored compounds, and thus to restore the legibility. For these reasons dye solutions are not regarded as suitable for use as 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. This does not happen to the incrustation from an iron ink. A liter of the standard writing ink of the Federal specification contains 29 g of nonvolatile solids, while the same volume of a dye ink may contain no more than 10 g of solids, and sometimes less. The standard red ink of the Federal specification is made by dissolving only 5.5 g of

<sup>37</sup> Government Printing Office Tech. Bul. 15, Standard Mimeograph Ink and Paper.

brilliant crocein  $M^{38}$  in 1 liter. A still weaker solution of methyl violet might 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 kept as 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 several decades. In some of the oldest account 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 this Bureau 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 pad, and when the sheet was torn off 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 writing, and it might be expected to fade quickly on that account. In spite of that, the copies are still of good depth of color, 39 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 circumstances. These remarks apply to the side of the thin sheets on which the copies are read. On the reverse sides, which were in direct contact with the original writing, the color is more intense.

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 made in this way 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. The use of "direct" dyes is another expedient. The results of some experiments with them will be found in the account of inks for recording instruments.

Many dyes have an antiseptic action, so their solutions do not become moldy, even 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 not otherwise thrive. No systematic work on this subject has been done by the Bureau. Anyone who is interested can easily make his own tests by inoculating the ink 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 the ink, but will do so on the cork of the bottle. A mixture of different species of mold spores can be obtained by slightly moistening a slice of bread, and then keeping it in a tight container to retain the moisture. In a few days the bread will be moldy, and a week or so later there will be an abundance of spores. If these are scraped off and dried without heating, they can be kept in

<sup>38</sup> In the Federal specification this dye is called "crocein scarlet 3B." It is also called "crocein scarlet MOO."

good condition a long time. A bit the size of a pinhead will contain a large number of spores.

Some dyes suggested for making colored inks are fuchsine, amidonaphthol red G, brilliant orange R, naphthol yellow S, tartrazine (yellow), malachite green, light green SF, yellowish, naphthol blue-black, diamine sky blue FF, soluble blue, Hofmann's violet, crystal violet, formyl violet S4B, Bismarck brown R, benzamine brown 3GO, direct deep black RW, extra, and nigrosine.

When a dye ink is used in a fountain pen, sometimes there is trouble from 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 glycerol (glycerin), which retains enough moisture to keep the dye from separating in solid form. If much more glycerol is added to the ink, it will dry too slowly on paper, and the writing easily becomes smudged. Indeed, if only one-tenth volume of glycerol is in the ink, 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 glycerol at the pen point.

#### (a) WASHABLE INKS

Now and then somebody asks how to make washable ink. In the only acceptable sense of the word "washable," such an ink is one that cannot be removed by washing; in other words, it is indelible. The inquirer, however, uses the word in exactly the opposite sense, because he wants to make ink which can be washed out of fabrics easily and completely. No study has been made of this subject by the Bureau, but in theory it is easy to make inks of this kind 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 dyes, so they are much used in dyeing, in order to fix the colors more lastingly to the fabrics. If a fabric is made of cotton or other vegetable fiber, the direct, or substantive, dyes should be avoided for these inks because they are taken up by the fabric directly, without the aid of a mordant. If the fabric is made of silk or of wool or some other animal fiber, the problem is far more difficult, because these fibers will take up dyes of almost any class.

#### (b) QUICK-DRYING INKS

Another question sometimes asked is how to make writing ink dry more rapidly on paper. Ink dries partly by evaporation and partly by being absorbed by the paper. Good writing paper is sized with rosin, glue, or other materials to keep watery solutions that are either neutral or slightly acid from being absorbed so rapidly that they will spread too much. In other words, the paper is sized in a way to keep ordinary writing inks, which are usually acid or neutral, from making blurred marks. A strongly alkaline ink will quickly show on the opposite side of the paper unless something is added to prevent this. How to keep an alkaline ink from spreading is told in Miner and Saylor's patent, discussed in the section on fountain-pen inks.

Alcohol evaporates more rapidly than water and also is absorbed more rapidly by paper. A small proportion of added alcohol will make ink dry more rapidly, but too much will make it penetrate paper and thin cards in an instant. How much alcohol can safely be added 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 drawing light, medium, and heavy lines with an ordinary pen upon scratch-pad paper and the bond paper used by the Bureau for letters. Another measured volume of alcohol was added and the mixture was tested as before. The addition of alcohol was continued until the lines were strongly feathered. With 10 volumes of blue-black gallotannate 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. The few drops removed for drawing each set of lines were negligible in comparison with the volume of the mixture.

Acetone is considerably more volatile than alcohol, and its effect upon red ink was tried. With scratch-pad paper there was more feathering than when an equal volume of alcohol was used, but on the bond paper there was none when 11 volumes of acetone was added to 10 volumes of ink.

In every case, beginning with the unmixed inks, the medium and heavy lines showed a slight 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 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, but a line was not considered as feathered unless its edges were noticeably uneven.

Ottley<sup>39</sup> patented a mixture of organic solvents to be added to writing ink to make it dry rapidly on paper. He stressed the fact that his mixture acts as a "penetrant," to carry the ink into the paper, yet said that the several ingredients "are rapidly and completely volatile." Two of the liquids have boiling points higher than that of water, but this is counterbalanced by their being good penetrants.

Realizing that the volatility of alcohol and acetone are drawbacks to their use in inks, some experiments were made at the Bureau with penetrants similar to one of those mentioned in the patent. It was found that the addition of enough penetrant to make the ink dry noticeably faster on paper also made it spread excessively in some kinds of paper. This is a difficulty that has not been done away with by the ink manufacturer. Ink that works well on really good, well-sized paper may be unsatisfactory on the cheaper grades. A postal card received from a correspondent asked why the ink had run on it. He thought the card was at fault, but a test made with five or six inks of different kinds showed that perfectly sharp lines could be drawn on it with some of them. The running, or blurring, was duplicated with two much-advertised inks.

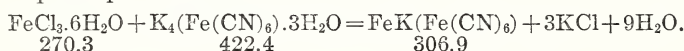
#### 4. PRUSSIAN BLUE INKS

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 sold as soluble prussian blue can be prepared. It does not form a true solution as sugar, salt, and many other substances do. It is more like

<sup>39</sup> G. B. Ottley, U. S. Patent 1,897,071, Quick drying Ink (Feb. 14, 1933).

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 mixed with it are removed. It is then soluble in water. The salts can be removed most easily by dialysis, because the blue when first precipitated soon so clogs an ordinary filter that water will barely pass through a thin layer of the pasty material. 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 toward 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 the ferrocyanide in order to get a good soluble blue. Perhaps the principal reaction is:



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, and "side reactions" as well. 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 of the composition shown in the equation; that is, it must contain 6 molecules of water of crystallization. This is dissolved in about 500 ml of water, and the solution is cleared by adding a few drops of hydrochloric acid. The solution should not be brown and cloudy, but of a clear, bright yellow. The weight of potassium ferrocyanide, which also must have the composition shown in the equation, will be 42.2 g, plus an excess of, say, 10 percent, or 46 to 47 g in all. This is dissolved in 1 liter of water in a 2-liter beaker. The iron solution is now 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 with distilled water. After the precipitate has been well 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 of blue 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. After the tying, the blue that adheres to the filter is transferred with the aid of a jet of water from a wash bottle. The sheet of Cellophane should be at least 20 inches square, and it must be wetted before it is made into a bag, or it may acquire incipient cracks which may permit the loss of the prussian blue if they develop into actual cracks.

When the blue has been transferred, the bag is hung in a 4-liter beaker, which is then nearly filled with distilled water. The water should come not quite up to the level of the mixture in the bag. Al-

though the excess of potassium ferrocyanide and the potassium chloride formed by the reaction pass out into the distilled water, some water also passes into the bag and may fill it if it is immersed too deeply. At the start of the dialysis, and occasionally during its progress, it is well to stir the mixture by jiggling the bag gently up and down while it is in the water. Failure to break up all the pasty lumps of blue has been the probable cause of an occasional failure to make satisfactory soluble blue by this method of washing. The water in the beaker should be renewed at least once a day for a week or 10 days. When it is suspected that the salts have been washed out, take out a drop of the liquid from the bag and let it dry without heating. Then put a drop of distilled water on the dry residue. If the prussian blue has been washed enough, it will at once dissolve in the water. Otherwise, the dialysis must be continued a few more days.

Thoroughly washed prussian blue will run through any filter, so the only way to get the dry substance is to hang the bag and its contents in a warm place for the water to evaporate. When it has dried 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 quickly. Attempts to hasten the drying by heating to the temperature of boiling water may cause much of the blue to become insoluble.<sup>40</sup>

Solutions prepared by dissolving 5, 10, and 15 g of prussian blue, prepared in the way just described, in 1 liter of distilled water, deposited only traces of sediment when kept in corked bottles for 7 years. During this time the solutions were in a dim light or in the dark, though this probably had no influence on the result. When a 5-percent solution in a bottle was exposed to summer sunlight for 56 days, there was no precipitation of the blue.

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. Oxalic acid is necessary to cause the commercial prussian blue to go into solution. 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. At this Bureau, the peculiar action of oxalic acid has been taken advantage of for preparing soluble blue from commercial prussian blue which did not dissolve sufficiently to color water. The finely powdered paint pigment was mixed with one-fourth its weight of oxalic acid and enough water to make a thin paste. After 24 hours the mixture was dialyzed in a bag of Cellophane. Without oxalic acid the dry pigment has not been made soluble by dialysis.

Writing done with prussian blue ink is very fast to light and to water and 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 destroy its color. Alkalies, even soap and water, decompose the blue and leave behind a rusty stain of iron oxide, which can be removed 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, a dye may be added to darken the shade and to produce what is sometimes called "blue-black ink." This name is unfortunately chosen,

<sup>40</sup> 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 cleared by adding oxalic acid.



because it is commonly understood to mean iron gallotannate ink made with a blue dye.

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 added to solutions of prussian blue and oxalic acid soon formed a gummy deposit. Three other black dyes, durol black *B*, Columbia fast black *FF*, and direct deep black *RW*, 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 gold-plated pen. It is suggested that those who are sufficiently interested 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 blue, the red and yellow will produce a practically black solution.

### 5. COLORED DRAWING INKS

In telling about carbon inks it was pointed out that black drawing ink is a colloidal suspension of carbon in a liquid. A few of the commercial colored drawing inks are suspensions of pigments in a liquid. These pigments are usually dye "lakes," formed by precipitating dyes on an inert material, for instance aluminum hydroxide, barium sulfate, or some other compound. Because the lakes are generally of greater specific gravity than carbon, and are not in such fine particles, the problem of grinding them so small that they will not settle to the bottom of the liquid is more serious than with carbon. The few pigment drawing inks examined by the Bureau had a decided tendency to settle. Nearly all colored drawing inks are clear solutions of dyes. They have comparatively little hiding power and show at their best when used on white paper. Their good working qualities outweigh the disadvantage of their transparency.

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 the colors 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 cannot 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 for waterproofing is a solution of borax and shellac. In this are dissolved 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 inks of seven colors required a great deal more work than has been anticipated. It did not suffice to use a more concentrated solution of shellac and borax in the same proportions as in the canceled specification. 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 which were extremely resistant to water. This was true if the chemical nature of the dyes made them combine with the shellac-borax film. Otherwise the dyes could be leached out. Only an outline of the work can be given here, and the reader is referred to the original article, which describes what was done.<sup>41</sup>

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 was 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 was then diluted to bring down the content of shellac 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.

This stock solution was used for making the actual inks, by mixing with it equal volumes of solutions of suitable dyes. Before use, the ink was filtered to remove any insoluble matter coming from the dye, or that had not been 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. Two bottles of each ink 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 added to an equal volume of the shellac solution, are listed in table 1. The dyes marked "second choice" made inks that did not keep quite so well as those 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 one of the two samples made with crystal violet. In this the color had been destroyed by a heavy growth of mold, but the duplicate was in good condition

TABLE 1.—*Dyes for drawing inks*

## FIRST CHOICE

Name of dye	In 100 ml	Name of dye	In 100 ml
	<i>Gram</i>		<i>Gram</i>
Erythrosine, yellowish.....	0.5	Wool blue G, extra.....	0.5
Brilliant orange R.....	.6	Methyl violet B.....	.5
Chloramine yellow.....	.4	Benzamine brown 3GO.....	.8
Brilliant milling green B.....	1.2		

## SECOND CHOICE

Brilliant crocein M.....	0.5	New methylene blue N.....	.4
Benzopurpurine 10B.....	.6	Crystal violet.....	.4
Orange R.....	.4	Benzo brown G.....	.6
Metanil yellow.....	.8		
Thiazol yellow.....	.8		
Malachite green.....	.8		

<sup>41</sup> E. W. Zimmerman, *Colored waterproof drawing inks*. Ind. Eng. Chem. 25, 1033 (1933).

## 6. RULING INKS

Ruling inks are used for drawing the lines on the pages of ledgers and other account books and on special forms of all kinds. There is a great dearth of published formulas for these inks. The formula given here was worked out by the Division of Tests and Technical Control, of the Government Printing Office. Two stock solutions are prepared, one containing 2 percent by weight of dye and the other a wax emulsion.<sup>42</sup> For use, 5 parts by volume of the dye solution is diluted with 15 parts of distilled water. Then 10 parts of the wax emulsion is diluted with 10 parts of distilled water, and is mixed with the diluted solution of dye. If the mixture has too strong a color, more of the diluted emulsion is added. The dyes used by the Government Printing Office are xylene cyanole *FF* for blue, and amidonaphthol red *G*.

A second formula makes use of the familiar solution of shellac and borax dissolved in water.<sup>43</sup> Dissolve 10 parts by weight of pale shellac and 2 parts of crystallized borax in 38 parts of boiling water. Separately dissolve 1 part of a basic dye in 48.6 parts of boiling water. Mix the solutions while hot, let cool, and add 0.4 part of 40-percent formaldehyde. The dyes suggested are fuchsine *A* and methylene blue *BB* extra. It may be added that shellac does not as a rule dissolve rapidly, and if there is any considerable quantity of it, the best procedure is to keep the water just below the boiling point, and to stir often, to break up the layer of melted shellac floating at the top. After some hours, when it is apparent that no more of the shellac will dissolve, let the solution cool and run it through fine muslin or a strainer, to remove waxy material and other solid impurities. If time is no object, it can be filtered through paper. Because the wax in it is sticky, the hot solution will clog the muslin or filter paper faster than the cold solution. Enough water to make up for what was lost by evaporation while the shellac was dissolving can now be added.

## 7. 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 section III, 5, and prepared in the same way. The requirements are much less exacting than for colored drawing inks, and numerous dyes in addition to those listed in table 1 can be used. In general, more dye than suffices for drawing ink will be needed.

Instead of dissolving dyes in the shellac-borax solution, dye lakes or other pigments can be ground with it to make a sort of water-color paint. It is hard to grind the mixture so thoroughly by hand that it will look smooth when brushed on paper. If a mortar and pestle must be used, add to the pigment only enough of the solution to make a thin paste, and when the grinding is done, dilute to the desired consistency.

<sup>42</sup> The emulsion used by the Government Printing Office is "water wax emulsion #311M," from the Franklin Research Corporation, 5134 Lancaster Ave., Philadelphia, Pa.

<sup>43</sup> H. Bennett, *Chemical Formulary* 4, 147. (Chemical Publishing Co., Inc., New York, N. Y., 1939.)



If the show-card ink need not be waterproof, a simple way to make it is to dissolve dyes in ordinary mucilage diluted with about 3 times its own volume of water. The gum in the mucilage prevents the spreading, or "feathering" of the ink on poorly sized cards. Pigments can also be used with the diluted mucilage.

Although the difficulty of preparing pigment inks has been pointed out, it must be said that in one respect they are superior to clear solutions of dyes. The pigments are nearly or quite opaque, and this gives the inks good hiding power, so that they show in their true colors on backgrounds other than white. Among the pigments that can be used are the metallic powders, or "bronzes," which are much used in paints.

White ink that can be used with a pen or a fine camel's-hair pencil is made by mixing a white pigment with a solution of gum arabic. A suggested formula is: Dissolve 20 parts by weight of gum arabic in 160 parts of warm water, and strain the solution through cheesecloth or a fine sieve to remove bits of bark and other solid impurities. For small quantities in the laboratory, the solution can be passed through a Gooch crucible. Mix with the solution 30 parts of titanium dioxide paint pigment and 0.5 part of sodium salicylate as a preservative.

Some of the colored pigments and all of the bronze powders are hard to wet with the solution of gum. This difficulty can be overcome by barely moistening the pigment with alcohol or acetone, and immediately adding the gum solution. A little of the gum may be precipitated, but will redissolve in a few moments when the mixture is stirred.

Many show cards are written with black ink, a typical formula for which is: Dissolve 16 parts by weight of asphaltum and 18 parts of venice turpentine in 50 to 60 parts of spirits of turpentine, and add 4 parts of lampblack.

## 8. EMBOSSING INKS

Embossing inks make raised characters, usually with a gold or silver luster.<sup>44</sup> The writing is done with a mixture of glycerol, 5 parts by weight; silicate of soda solution ("waterglass"), 2 parts; water, 8 parts; red, green, or violet writing ink, enough to color so that the writing can be seen easily. The glycerol keeps the writing from drying too soon, and the silicate of soda forms the raised writing, as will be explained. While the writing is still moist it is dusted with a "bronze" powder or with any other pigment that will withstand the subsequent heating in contact with the alkaline silicate. The excess of powder is removed by flicking the back of the paper with the fingers. The writing is raised by heating the back of the paper to a temperature below charring, yet high enough to turn the moisture in the ink into steam. This puffs up the pasty silicate and dries it, so that it becomes quite hard and remains so indefinitely. Most of the glycerol is absorbed by the paper, but part of it is driven off with the steam. A convenient way to heat the back of the paper is with an electric iron arranged with the flat side uppermost. The paper is pressed against it with a fork or other suitable instrument. After the paper

<sup>44</sup> The greater part of this paragraph is adapted from H. Bennett, *Practical Everyday Chemistry*, p. 141. (The Chemical Publishing Co., Inc., New York, N. Y., 1934.)

has become cool, it is wiped with a soft cloth to remove any loose bits of pigment.

#### 9. STENCIL INKS

Stencil inks are for marking on bales, boxes, and other surfaces, usually with the aid of a stencil, but sometimes with only a brush. Some of them are liquids and others solid cakes from which a moistened brush takes up the desired amount of color.

One of the simplest stencil inks is made by mixing spirits of turpentine with enough lampblack to give a good color. The turpentine readily sinks into wood and carries with it enough of the lampblack to make marks that cannot be removed readily by rubbing.

Some of the published formulas require a solution of borax and shellac in water, like that used for show-card inks. Dyes are dissolved in this solution, or pigments are dispersed in it. One example is to dissolve 4 parts by weight of dry orange shellac and 1 part of borax in enough water to make a solution like thin sirup. Ink made by this formula is reasonably resistant to water, unless the surface on which the marks are made is so porous that most of the liquid is absorbed, and not enough to bind the pigment is left.

Among the uses of stencil inks is the putting of slogans on sidewalks during municipal "drives." A cheap ink for this purpose, as well as for marking boxes and bales, can be made by the following formula,<sup>45</sup> in parts by weight: Mix intimately plaster of paris, 40; pigment, 30; dextrin, 15; and then add water, 15. This mixture is allowed to harden in a shallow box of suitable size. The ink is used with a stencil brush wet with water. Among the pigments that can be used are carbon black, ultramarine blue, chrome green, chrome yellow, toluidine red, and any of the so-called permanent organic toners or lakes. Because of differences in the specific gravities of pigments, their fineness of grain, and their color strength, a given weight of one will not be equivalent to the same weight of another. For this reason the formula cannot be adhered to strictly.

#### 10. HECTOGRAPH INKS

The hectograph is a simple device for making a number of facsimile copies of a letter or a drawing. The original is written with a special ink that is heavily loaded with a water-soluble dye. When dry, it is pressed into intimate contact with a prepared surface of gelatin (or glue) and glycerol, or of clay and glycerol. This surface absorbs part of the ink of the original, and can then be used for printing upon other sheets of paper. Generally the gelatin-glycerol mixture is poured into a shallow pan, where it sets to a moist elastic mass on cooling. The clay-glycerol mixture is like stiff putty, and must be pressed and rolled to a smooth surface. The printing is not always done by hand, but sometimes by special machines, with the gelatin-glycerol composition in a thin layer on a roll of paper.

Hectograph ink must contain a large proportion of a dye that has good color strength. In experiments at this Bureau, a number of different dyes were made into hectograph inks, in order to find out which of them gave the greatest number of satisfactory copies. The inks were made by a formula obtained from the United States Gov-

<sup>45</sup> From the Division of Tests and Technical Control, U. S. Government Printing Office.

ernment Printing Office, except that in it acetone was substituted for alcohol. The formula, in parts by weight, is:

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

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

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, if it clings to the bottom of the container 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 inflammable and quite volatile, but the amount in the ink is not dangerous. If it should be poured into the hot solution of dextrin, there would be 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 when dissolved in the stock solution just described. The best dye of all was methyl violet *B*, but crystal violet was almost as good. For red ink, rhodamine *B* was first choice, and fuchsine (magenta) second. 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, brilliant green and victoria blue *B* ranked first, with malachite green and soluble blue second.

There is no truly black water-soluble dye, for dilute solutions of all the so-called black dyes are blue or purplish. Hectograph ink containing water-soluble nigrosine will make one or two nearly black copies, but the succeeding ones are of 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 or by the sheets 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 was almost illegible on white paper, on account of an interesting optical effect. Its brightness was almost the same as that of the white paper. Because of that there was no great contrast between it and the paper, and the copies looked so much blurred as to be illegible. When seen through blue glass, which made the ink look dark, the copies were sharp and distinct.

In various books there are simpler formulas for hectograph ink than the one that has been given, but they have not been tested by the Bureau. In these formulas all parts are by weight:

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

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

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

*Red*.—Fuchsine, 1; glycerol, 1; water, 5; alcohol, 1.

*Violet*.—Methyl violet *B*, 1; glycerol, 2; water, 7.



## 11. STAMP-PAD INKS

## (a) ORDINARY STAMP-PAD INKS

Federal Specification TT-I-556, for stamp-pad ink, originally gave a formula for a standard glycerol-base ink in five colors. The amendment of January 1940, gives formulas for ordinary, or slow-drying, and for quick-drying inks. The ordinary ink is made by dissolving dye in a mixture of equal volumes of U. S. P. glycerol and distilled water. The dyes for the standard inks and the amount of each to dissolve in 1 liter of the solvent are: Nigrosine, 48 g; soluble blue, 24 g; light green *SF*, 32 g; fuchsine (magenta), 16 g; crystal violet, 16 g. These amounts of dye are all smaller than were required in the original specification, and crystal violet is substituted for methyl violet. The specification in its original form did not take into account that dyes differ greatly in color strength.

At ordinary temperatures glycerol is practically not at all volatile, and it is hygroscopic, or attracts moisture from damp air. This keeps the ink from drying on the pad, even in winter, when the air in heated buildings may be of desert aridity. In summer, when the air is of high humidity much of the time, the ink takes up water, and sometimes the pad is too wet. Special evaporation tests showed surprisingly large changes in the amount of water held by glycerol as the relative humidity of the air varied from day to day. A 2-g sample of a mixture of equal volumes of glycerol and water was exposed to the air in a flat-bottomed dish of such a size that the layer of liquid was about 1 mm deep. In such a shallow layer it quickly responded to changes in atmospheric humidity. According to an approximate calculation, the 2 g of the mixture contained 933 mg of water at the start.<sup>46</sup> In 2 weeks of rather low humidity, it lost 882 mg in weight, or 94.5 percent of the original water. The residual glycerol was not far from being as concentrated as it was before being mixed with the water.

## (b) QUICK-DRYING STAMP-PAD INKS

Because ordinary stamp-pad inks do not dry rapidly, unless the paper is unusually absorbent, when numerous impressions are made in quick succession there is danger of smearing or even obliterating them. Various formulas have been devised for inks that will dry quickly on paper. Some are made with oils, which may injure the rubber stamps. Another idea is to add a "penetrant" to a glycerol ink, to make it sink into paper rapidly. Some of the commercial quick-drying inks that have been tested by the Bureau contained ethyl acetate as the penetrant, and some of the published formulas call for alcohol. These liquids are effective, but they are much more volatile than water and evaporate from a stamp pad in a comparatively short time. This is the more likely because many persons leave stamp pads open to the air all the time. An evaporation test like that in the preceding section was made on a mixture of 2 volumes each of glycerol and water and 1 volume of 95-percent alcohol. The total weight of water in a 2-g sample of the mixture was calculated as being close to 1,100 mg. In 2 weeks the loss of water and alcohol was 1,055 mg.

<sup>46</sup> The calculation is based upon the specific gravity of U. S. P. glycerol and its content of water.

It seemed obvious that whatever penetrant was used should have as high a boiling point as possible, so that it would stay in an exposed stamp pad a long time. A penetrant that met this condition admirably was found in the monobutyl ether of diethyleneglycol. Its boiling point, 231° C (449° F), is far higher than that of water, 100° C (212° F). Evaporation tests were made on a 2-g sample of a mixture of 2 volumes each of water and glycerol, and 1 volume of the ether, and on a 2-g sample of ink made by dissolving fuchsine in the mixture. In 2 weeks the mixture without dye lost by evaporation of water and ether a total of 812 mg, while the dye solution lost 809 mg. It was calculated that 2 g of the mixed solvents contained 770 mg of water. The dye solution contained slightly less water. Evidently but little of the butyl ether evaporated.

With these and other experiments, a formula for a satisfactory quick-drying ink was worked out.<sup>47</sup> Too large a proportion of the butyl ether added to a solution of dye in a mixture of glycerol and water will cause the ink to make blurred impressions. If too little is used, the impressions will not dry quickly enough. Regardless of the amount of water, which varies according to the atmospheric conditions, there should be 1 volume of the monobutyl ether of diethyleneglycol and 2 volumes of glycerol. To turn the slow-drying ink of the preceding section into quick-drying, all that is necessary is to add to it one-fourth its volume of the butyl ether. The color will not be so intense, because the solution of dye is thereby diluted to four-fifths of its original concentration.

In a very dry atmosphere it may be desirable to use a mixture of 2 volumes of glycerol and 1 volume of water, with 1 volume of the butyl ether. If the ink contains the larger proportion of water, a freshly inked pad may need a further inking after a day or two, because so much of the water evaporates. After this reinking, the pad should require no further attention for a long time.

The amendment to Federal Specification TT-I-556, Ink; Stamp pad, provides for the purchase of quick-drying ink. The standard inks with which purchases are to be compared are made with the same dyes, in the same amounts, as for the slow-drying inks (see preceding section). The dyes are to be dissolved in a mixture of 2 volumes each of U. S. P. glycerol and distilled water and 1 volume of Butyl Carbitol.<sup>48</sup>

When this ink is applied to a brand-new pad, it sinks in at once. Ink made with glycerol and water, without a penetrant, may stay on the surface of a new pad for many seconds before the fabric is wetted through and the ink can sink into the felt in the pad. Impressions made on paper, except some special, heavily sized kinds, dry almost at once. If the pad is properly inked, so that the rubber stamp is not made too wet, it is hard to be quick enough to smear the impressions by rubbing them with the fingers after they are made. A pad can be left open to the air for months without losing enough of the butyl ether to make the ink slow-drying.

<sup>47</sup> C. E. Waters, *Quick-drying stamp-pad inks*, J. Research NBS 20, 543-547 (1938) RP1087. Patent No. 2,208,551, July 16, 1940, has been assigned to the United States Government. Those who wish to make the ink for sale should apply to the Secretary of Commerce, Commerce Building, Washington, D. C., for a free nonexclusive license to use the formula.

<sup>48</sup> Butyl Carbitol is the trade-mark of the manufacturers of the monobutyl ether of diethyleneglycol.

## (c) INKS FOR WOODEN STAMP PADS

The idea of making stamp pads of wood, instead of felt covered with a thin cotton fabric, is not new. A nonresinous wood with fine pores is cut across the grain into slabs of the thickness of the usual felt pad. The surface against which the rubber stamp is pressed to ink it is finished smooth. Ink is quickly taken into the pores of the wood, and two or three drops put in one spot will soon show on the opposite face of the pad, because the pores are tiny tubes that run through the wood in the direction of the grain. Ink does not spread to any extent at right angles to the pores (that is, across the grain), because in order to do so the dyes would have to pass through the semipermeable walls of the cells of the wood.

The surface of a fully inked pad looks too dry to be of any use, yet it will ink a rubber stamp well enough to make sharp impressions of good color. The chief fault of a wooden pad is that when the ink at the middle is exhausted, there is no inflow of ink from around the edges to the center. This is not true of the ordinary felt pad, in which the ink distributes itself uniformly. In other words, there is good "recovery" in a felt pad but almost none in a wooden one.

Several inks intended especially for use on wooden pads have been patented, though almost any stamp-pad ink can be used. The quick-drying ink described in the preceding section works well on a wooden pad. Possibly all the inventors of the special inks had in mind the idea that these were necessary to keep the wood from warping. This is definitely said in the abstract of one patent.<sup>49</sup>

## 12. INKS FOR RECORDING INSTRUMENTS

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 on 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 that will not dry on the pen, if the record is made 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 glycerol 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 added to the ink. For indoor use, a mixture of one volume of glycerol and three volumes of water has been found to make satisfactory recording ink.

The properties of glycerol that make it so valuable in recording and stamp-pad 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 have "feathered" or uneven edges. The ink spreads in all directions from the actual marks made with the rubber stamp or the pen and does not just go down into the paper. Whether or not the ink feathers depends upon the paper or card, 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 pre-

<sup>49</sup> See Chem. Abstr. 29, 5682 (1935) for abstract of a British patent issued to Arthur L. Glover. In the same journal, 26, 4069 (1932); 32, 1498 (1938), are abstracts of patents issued to Josef Ehrlich and to H. Krotoschin, respectively.



pared by dissolving selected dyes in glycerol and water in the proportions for both outdoor and indoor recording inks. Inks were also made with similar mixtures of ethyleneglycol and water, because the glycol is in so many respects like glycerol, though somewhat more fluid.<sup>50</sup>

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 glycerol and water already mentioned. Because very little of each ink was needed, 0.1 g of dye was dissolved in 10 ml of liquid. Lines were drawn on 5 kinds of paper, including 3 heavy papers, or thin cards, furnished with recording instruments. They 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), or *F* (decided feathering). The results showed that neither the acid nor the basic dyes could be considered as the better. Of the total 190 sets of 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 by forming insoluble compounds. It was thought that perhaps the direct dyes would not spread in the paper when the glycerol and water were absorbed, and for that reason the lines would have smooth edges.

In all, 16 direct dyes were made into 64 inks, by dissolving them in the 2 mixtures of glycerol and water and in equally diluted ethyleneglycol. Except for a few special tests, each ink was made by dissolving 0.1 g of dye in 10 ml of liquid. As before, lines were drawn on 5 kinds of paper and were rated in the same way. The table of results leads to 3 general conclusions: Inks made with direct dyes feather much less than those made with acid and basic dyes; glycerol at either dilution is a better solvent than equally diluted ethyleneglycol; and, as might have been predicted, the greater the proportion of water in the ink, the less is its tendency to feather.

TABLE 2.—Feathering tests of inks made with direct dyes

Rating <sup>1</sup>	Glycerol-water		Glycol-water	
	1 : 1	1 : 3	1 : 1	1 : 3
Total <i>N</i> .....	52	79	27	69
Total <i>SF</i> .....	21	1	15	11
Total <i>F</i> .....	7	0	38	0

<sup>1</sup> *N* means no feathering; *SF*, slight feathering; and *F*, decided feathering.

It is not necessary to give the names of the acid and basic dyes used in the first series, but the list of direct dyes may be of some interest. There are 17 dyes in the list, but the yellow one was not rated and does not show in the summary of results in table 2. Its pale color and brightness made so little contrast with the paper that

<sup>50</sup> C. E. Waters, *Inks for recording instruments*. J. Research NBS 17, 651-655 (1936) RP935.

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.

TABLE 3.—*Direct dyes for recording inks*

<i>Red</i>	<i>Violet</i>
Benzo fast scarlet. Congo red.	Diamine violet N. Oxamine blue 4R (Erie violet 2B).
<i>Orange</i>	<i>Brown</i>
Toluylene orange R. Toluylene orange G. Pyrazol orange.	Bismarck brown R. Benzamine brown 3GO.
<i>Yellow</i>	<i>Black</i>
Chloramine yellow.	Columbia fast black FF extra. Direct deep black RW extra (Erie black RXOO). Direct deep black RW extra (Erie black RW). <sup>1</sup>
<i>Green</i>	
Chloramine green E. Diamine green B.	
<i>Blue</i>	
Diamine sky blue FF. Benzo sky blue.	

<sup>1</sup> The 2 samples of direct deep black extra were from the same manufacturer and were labeled with the names in the parentheses. One gave a deeper color than the other when dissolved in the same concentration. All the dyes were dissolved at the rate of 1 g in 100 ml of solvent.

One of the dyes, toluylene orange R, did not make a clear solution, so it might cause trouble by clogging the pen. Another of the dyes, diamine green B, set to a sort of soft jelly overnight, but this became quite fluid when shaken, and it then flowed freely from the pen. The two green dyes made inks of a rather dull color.

When the inks made with direct dyes had been kept in corked tubes for 12 weeks, some of the corks were moldy. Of the inks made with equal volumes of glycerol and water, 6 had moldy corks. With the more dilute glycerol, 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 ethyleneglycol, at either dilution. It might be concluded that the glycol is a better preservative than glycerol, but this would have to be confirmed by further experiments.

Sometimes when the line drawn on a chart is not sharp, the paper and not the ink is at fault. This is apt to be true when the line is on a long strip of paper. The paper is sometimes so thin that it will not hold the ink without its spreading laterally, and this will make a feathered line. There seems to be no complete remedy for this, but it helps if the ink contains a large proportion of water that can evaporate, if the opening in the pen is as small as possible, and if the paper rapidly travels past the pen.

If the line of the record is a series of dots, each made with a quick touch of the pen to the chart, it might be an advantage if the ink contained a small amount of a penetrant to make the dots dry sooner. Too much penetrant would make the dots too large. A quick-drying ink cannot be used if the pen draws a continuous line, because the pen will be drained rapidly and the line be a blur.

## 13. 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 in books, nearly all are for inks made with silver, or are of the aniline black type.

Although silver inks look black in the bottle and make moderately dark marks on white fabrics, their full color must be developed by heat or by direct exposure to sunlight. Either treatment reduces the silver salt, 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.<sup>51</sup>

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 1 fluid ounce of ink. This formula has been used for a number of years by an institution in the District of Columbia, where the laundering conditions are severe, and where other inks had been found unsatisfactory.

"Household" ammonia is not suitable, as a rule, because it contains 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 actual alkali of 3.0 parts of the anhydrous salt. The small additional quantity of water, 0.5 part, thereby added will make no noticeable difference in the ink.

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 in water and 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 will be needed to darken the mixture. This final step in the preparation of the ink is really 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 and let it stand awhile.

Because of the chemical action of steel upon silver ink, a gold pen, or a quill pen, if it can be had, should be used. 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 have no advantage over black ink. In fact, the silver in the ink soon turns the marks black and the dye washes out.

<sup>51</sup> Guiller, Dinglers polytech. J. 1851, 70.



Inks containing gold, platinum, or osmium have been recommended for marking fabrics. A striking property of a dilute water solution of osmium tetroxide, often called osmic acid, is the ease with which organic matter reduces it to the metal or to a black lower oxide. It is not necessary to heat the marks nor to expose them to sunlight. It is dangerous for an inexperienced or incautious person to handle osmium tetroxide, because it is so volatile, and its vapors are poisonous and act strongly on the moist tissues in the nose and on the eyeballs. Fortunately, osmium tetroxide is so expensive that it is not likely to be used for indelible laundry ink.

Gold and platinum are more resistant to chemical reagents than silver is, and their salts, like those of silver, are easily reduced and blackened by organic matter. When solutions of these metals are used for marking, the fabric is first sized with a solution of gum arabic and a reducing agent. The following formulas are selected from those found in books.

Platinum ink is made by dissolving 1 part by weight of chloroplatinic acid (often called platinum chloride) and 2 parts of gum arabic in 10 parts of water. The fabric is treated with a solution of 3 parts of oxalic acid, the reducing agent, and 3 parts of gum arabic in 10 parts of water. Let the cloth dry before writing on it, and after the writing has become dry, wash the cloth thoroughly.

Gold ink is a solution of 1 part of sodium chloroaurate and 1 part of gum arabic in 10 parts of water. The reducing agent is stannous chloride ("tin salt"), 1 part of which and 10 parts of gum arabic are dissolved in 100 parts of water and used to size the fabric. Because stannous chloride gradually oxidizes in the air and loses its power to reduce gold salts, the treated fabric should not be kept too long before writing on it. The writing soon turns to a purplish brown. When it is dry, the fabric must be well washed.

Possibly the oldest marking ink containing a metal, or for that matter, of any other composition, is described by Mitchell.<sup>52</sup>

Aniline black is extremely fast to washing and to light, so it is suitable for making indelible ink. Possibly some of the water-insoluble forms of other black dyes are also used in commercial indelible inks. The Bureau has never made inks of either kind, and rarely receives indelible inks for test. The formula about to be given is typical of those for the development of aniline black in and on the fibers of fabrics. 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 ("Aniline salt").....	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.

<sup>52</sup> C. A. Mitchell, *An Ancient Egyptian marking ink*, Analyst **65**, 100-01 (1940). Pieces of linen found in a tomb which probably is of an earlier date than 2980 B. C. were marked with iron oxide.

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

An aniline black ink which has been recommended for use with a rubber stamp is made as follows: Grind separately, and as fine as possible, 20 parts of copper sulfate crystals (bluestone) and 30 parts of aniline hydrochloride. Mix the two, add 10 parts of dextrin, 5 parts of glycerol, and then water in small portions until the mass has the right consistency.

An interesting development of recent years is an indelible ink that is visible only when illuminated with a lamp that gives a great deal of ultraviolet radiation. The marks then glow with a bright fluorescence that is in good contrast with the background of unmarked fabric. The Bureau is unable to give any information about the composition of these widely used inks. Abstracts of three patents have been published.<sup>53</sup> It is not known whether the same ink is referred to in a short note published at about the time the British patent was granted.<sup>54</sup> The patentee is said to be a British firm, but the firm named in footnote 53 is American. Among the materials mentioned in the article are several inorganic compounds, most of them minerals. The only binders to hold the other materials to the fabric are gum arabic and albumen, neither of which would seem to be able to resist even mild washing.

#### 14. SYMPATHETIC OR INVISIBLE INKS

Persons who indulge in secret writing for legitimate or nefarious reasons must have invisible or sympathetic ink. In his chapter on this subject, Mitchell<sup>55</sup> says that both Ovid (43 B. C. 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 characters become visible. These are but two examples of secret inks that are made visible by heating. Some 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

<sup>53</sup> The three patents are U. S. Patents 2,073,381 and 2,086,745, granted to Francis M. Sell in 1937; and British Patent 462,013, to the National Marking Machine Co., March 1, 1937. (See Chem. Abstr. 31, 3181, 6026, 6484 (1937).)

<sup>54</sup> American Ink Maker 15, 37 (March 1937).

<sup>55</sup> Page 336 of the book cited in footnote 1.

above a small flame. This is as good a sympathetic ink as any, is not dangerously poisonous, and is easy to prepare.

The salts of several metals have long been favorite materials for sympathetic ink. Some of the salts are not colorless when in solid form or in strong solution, but invisible marks can be made on paper with very dilute solutions and developed by suitable means. Among these salts are lead acetate, ferric sulfate, copper sulfate, cobalt chloride, and nickel chloride. In addition to being turned brown or black by the fumes of ammonium sulfide, the writing can be developed by heat, and still other means can be employed with some of them. For instance, if the ink is a solution of ferric sulfate, a solution of gallic or tannic acid will turn the writing black, and potassium ferrocyanide will convert it into 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 a solution so dilute as to be only of a moderately deep pink is used as sympathetic ink, the thin deposit of the crystals that are left on the 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 on 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, and they have been taken advantage of in the so-called "barometer paper" for predicting changes in the weather. If the secret writing should be heated too strongly when warming it to turn it blue, the chloride will cause the paper to char, and the writing will then be permanently black.

If a drop of water is put on a sheet of writing paper, the wet spot will look dark against a dark background, because wet paper lets more light pass through than dry paper does and reflects less light back to the eye. A sympathetic ink based upon this principle is made by vigorously shaking together 1 volume of linseed oil, 20 volumes of ammonia water, and 100 volumes of distilled water. The alkaline ammonia turns part of the oil into soap, which emulsifies the rest of the oil. When the creamy emulsion is used for writing, the oil forms a film on the paper and soon hardens by oxidation, instead of spreading through the paper as a nondrying oil would do. When the writing is dipped into water, the oil film keeps the writing from becoming wet, and as a result it stands out in light characters against a dark background of wet paper.

As a means of developing writing done with a variety of inks, iodine is interesting. It is preferably applied as the vapor given off by the crystals at ordinary temperatures, though the tincture diluted with water can be employed. If a thin solution of starch boiled with water was used for writing, the 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 the paper does. This color soon vanishes because iodine is so volatile. Copper sulfate and lead acetate are colored temporarily. 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 there more readily than elsewhere.

Inks which give writing that disappears in a short time are sometimes called "vanishing" inks. Some of these have been mentioned, and two more may be added. Dilute solutions of copper sulfate (blue) and nickel sulfate (green) give invisible writing on white paper. When exposed to the fumes from ammonia water, the copper sulfate is converted into a dark-blue compound, and the nickel sulfate into a similar but less strongly colored compound. On exposure to the air the ammonia escapes, and the writing is again invisible.

Once or twice a year the Bureau is asked to recommend an ink that will fade away within a few hours or days. The correspondents who ask for information about inks of this kind evidently have in mind inventions that will be of no value without the right ink. Unfortunately there seem to be no inks that can be depended upon to vanish so accommodatingly, at a predetermined time.

In the discussion of indelible marking ink for fabrics a new kind was described which glows under ultraviolet radiation, but is invisible in ordinary light. This glowing, which ceases when the material is removed from the influence of the ultraviolet, is called "fluorescence." Many substances besides those used for the indelible ink are fluorescent, and those which are soluble in water might be used as sympathetic ink. One of the easiest of these substances to obtain is quinine sulfate. As little as 0.1 g of the sulfate dissolved in 1 liter of water to which 3 or 4 drops of concentrated sulfuric acid has been added shows blue fluorescence. A 1-grain quinine pill would make 1.4 pints of solution.

The hydrocarbon anthracene, unless it is too impure, gives brilliant green fluorescence. It is insoluble in water, but dissolves to a moderate extent in ethyl alcohol, and somewhat more in acetone, but neither solution is suitable for writing on paper. It has been pointed out on an earlier page that alcohol and acetone almost instantly spread in all directions in paper, and that only blurred, illegible writing can be done with ink which contains a large proportion of either of these solvents. The Bureau has found that an easily prepared emulsion of anthracene can be used as ink. Dissolve a little anthracene, say about 25 mg, in 10 ml of acetone, preferably in a wide-mouthed bottle. Pour into the solution all at once, and quickly, 25 to 30 ml of water. This will precipitate the anthracene in such finely divided form that it will remain suspended in the liquid for days. This emulsion can be written with, and when it dries, the particles of anthracene cling to the paper. They cannot be seen on white paper. If the water is not added quickly enough to the acetone solution, part of the anthracene may be precipitated in lumps, which will not break apart when the mixture is shaken.

Every now and then someone writes for information about a secret ink that is visible only when looked at through a special screen. The Bureau has not worked on inks of this kind, and can give no formulas, but anyone with sufficient time and patience can make an ink that will exactly match a particular colored paper. If the same dyes are not used for both the paper and the ink, the writing will be visible when looked at through a screen of a suitable color. The theory of this is simple enough.

Suppose the paper and ink are of the same shade of red to the unaided eye. If the light that comes to the eye from the paper is analyzed with a spectrophotometer, it will be found that it is made up of red and other colors in different proportions. The sensation of red in the eye is the resultant of the effects of all these colors acting upon the retina at the same time. If the light from the ink is analyzed in the same way, it will also be found to consist of a mixture of colors, and unless the same dye happened to have been used for coloring the paper and making the ink, the mixture of colors from the ink will not be the same as that from the paper. If the writing is looked at through a colored screen, for instance blue glass, parts of both red lights will be absorbed, and parts will pass through the blue glass. In general, after passing through the blue glass the light from the paper will not produce upon the eye the same sensation as the light from the ink. In other words, they will appear to be of different colors, and for that reason the writing will show upon the paper. It may require a long series of experiments, mixing dye solutions in different proportions, to make an ink that exactly matches a given piece of paper.

In examining a document suspected of containing secret writing, the first step would be to try the effect of ultraviolet radiation, because it will not interfere with subsequent tests that may be made, and because it may cause the secret writing, if any, to glow with a 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 bring out nothing, but any latent writing is not apt to be destroyed by the treatment. Exposure to iodine vapor might be next in order, then the fumes from ammonia water, followed by the fumes of ammonium sulfide. If all of these fail, chemical solutions must be tried on selected parts of the document. To treat the whole paper with a solution that brought no visible result might destroy all chance of developing the writing with something else. 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. It is safest to do this in a letterpress with white cloths or white blotting paper moistened with the solution. In this way a minimum of water will be used. If the secret writing was done with an easily soluble substance, dipping the paper into, or brushing it over with, the solution might dissolve the invisible substance and thus destroy the evidence. In a letterpress, unless the cloths are too wet, there is little flow of liquid, and the danger of hopelessly blurring the writing is reduced to a minimum.

#### 15. INKS FOR SPECIAL MATERIALS

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

## (a) INKS FOR CELLULOID AND OTHER PLASTICS

The synthetic plastics are a large group of materials of most diverse chemical composition, which, with few exceptions, have become important commercial products only within the past 10 or 15 years.<sup>56</sup> There is a great mass of literature on the group, and a periodical is devoted to them. The oldest and best known of them are celluloid and the related materials derived from cellulose nitrate. Another familiar plastic is Bakelite, to which are related similar materials classed as phenol-formaldehyde resins. If this were the place for it, many more examples could be given of materials quite unlike these two in chemical composition.

Inks are used on so many things that it is to be expected that inks for writing or stamping on the various plastics are of interest to some persons. In general these inks cannot be made with water, because the plastics are nonporous and resist penetration by water. If the ink should happen to write well on the plastic, it would make marks that are easily removed by slight rubbing with a damp cloth. In order to make reasonably permanent marks the ink must contain a liquid that is readily absorbed by the plastic. The best liquid for making the ink is a solvent for the plastic on which the writing or marking is to be done. If the plastic happens to be insoluble in all liquids that are available, there is not much hope of making a good ink for use on it. The plastics are colloids, and when they dissolve, they behave like glue, the typical colloid, when it is put in water. The solid starts to absorb the liquid and at first is merely tacky on the surface, but as the liquid penetrates more and more, the solid plastic swells and becomes softer and softer. At the final stage the solid has taken up all the liquid, and the liquid is evenly distributed through the solid. According to the amounts of solid and liquid, the final stage may be a jelly, a very viscous liquid, or a perfectly fluid solution.

It is easy to see that if an ink is made by dissolving dye in a solvent for a given plastic, the swelling and absorption can proceed just as if there were no dye. The only essential difference is that at least part of the dye will be absorbed by the softened plastic and will make permanent marks when the solvent evaporates or penetrates further into the solid. Fortunately, most of the dyes are colloids when in solution and they cannot penetrate far into the colloidal plastics, and as a result the ink will make sharp lines with little feathering.

For writing or stamping on plastics it is desirable that the ink shall not dry on the pad too rapidly. This debars a few solvents that might otherwise be used on some plastics. Experiments were made with inks prepared by dissolving 0.16 g of crystal violet in 10 ml of each of the following solvents, whose boiling points range from about 124° C (256° F) to 231° C (448° F), or well above the boiling point of water, 100° C (212° F). The solvents were the monomethyl ether of ethyleneglycol (I), and the monomethyl (II), monoethyl (III), and monobutyl (IV) ethers of diethyleneglycol. For brevity the roman numbers will be used in discussing the results of the experiments. All but three or four of the plastics were in rectangular pieces 1 by 3 inches, and ranging from about one-thirty-secondth to one-eighth inch in thickness.

<sup>56</sup> G. M. Klire, *Organic Plastics*, Cir. NBS C411 (1936).



On each sample of plastic the code letters were written and two or three short lines were drawn with each ink, all with a gold pen. The results are summarized below.

Only a comparatively small number of kinds of plastics were available, and on four of these none of the inks dried in as short a time as 5 minutes. These four plastics were vinyl chloride-acetate, methyl methacrylate, phenol-formaldehyde, and urea-formaldehyde.

Ink made with solvent I dried in 1 minute on cellulose nitrate, acetate and acetobutyrate, and on ethylcellulose, and in about 5 minutes on casein-formaldehyde. Solvent II made ink that dried in 2 or 3 minutes on cellulose nitrate, acetate, and acetobutyrate. Ink containing solvent III also dried in 2 or 3 minutes on these three compounds of cellulose, and in less than 5 minutes on ethylcellulose. Ink with IV as the solvent dried within 1 minute only on cellulose nitrate and ethylcellulose.

According to the plastic, the solvent, and the heaviness of the strokes of the pen, the time required for drying ranged from 1 minute to 18 hours (overnight), and in one case to 42 hours. In some cases the ink did not properly wet the surface of the plastic, but drew up into droplets like beads along the strokes of the pen. In a number of other cases, particularly with IV, the ink spread over the surface of the plastic in a thin film that did not dry overnight. IV also caused crazing of the surface of two of the samples of methyl methacrylate.

#### (b) INKS FOR VARIOUS COATED SURFACES

Plastics are not the only materials for which special inks may be needed, because it is sometimes desired to mark on varnished and other coated surfaces. From time to time the Bureau is asked what to use, and can sometimes, but not always, give the right answer. Whether or not a particular ink will dry on a given surface in a reasonably short time depends upon circumstances similar to those discussed in the section on inks for various plastics. In order to get some information on the subject, a series of tests was made on small panels of tin plate coated with various paints, varnishes, and lacquers, on baked enamels of the kind seen on office filing cases, two kinds of paper that had lithographed designs covered with a lacquer, and heavily oiled cardboard ("stencil board").

The inks were those used on the plastics in the preceding section and two or three others. In some cases the marks were made with a pen, and in others impressions were made with a rubber stamp inked on pads which were simply small squares of blotting paper saturated with the inks. Writing with a pen is the more severe test of the drying quality of the ink, because more of it is put on the surface than when a rubber stamp takes a film of ink from the pad, and transfers only part of it to the surface being tested. If the writing dries in a few minutes, it is practically certain that impressions made with the rubber stamp will take no longer.

The results varied as much and in about the same ways as the tests made on the plastics. Ink made by dissolving a dye in the monomethyl ether of ethyleneglycol dried most quickly on the greatest variety of materials. The only surface on which it did not dry within 2 or 3 minutes was one of the two samples of lithographed and lacquered paper, but no liquid was found that would sink into this surface.

One of the Departments needed an ink for marking on photographs, made on bromide paper, and had found that ordinary stamp-pad ink dried so slowly as to be a handicap. The quick-drying stamp-pad ink made by the Bureau's formula was also of no value, because it spread badly on the surface and did not dry rapidly. It was found that a mixture of one volume each of glycerol and water, and one-half volume of the monomethyl ether of ethyleneglycol made very satisfactory ink. Because an extra-bright red was wanted, crocein scarlet *SB* was used in this, instead of fuchsine.

The best ink for stamping on a large number of oiled stencils was another problem. The ink recommended was made by dissolving fuchsine in a mixture of two volumes of glycerol, one volume of water, and two and a half volumes of the monobutyl ether of diethyleneglycol. The greatly increased proportion of penetrant made the impressions dry in a few minutes, except on some of the oilier spots on the stencils. Quick-drying ink made by the Bureau's regular formula was almost nondrying.

There were two small pieces of steel with baked enamel on them. The four inks used on the plastics were tried on these enamels. On one, the ink made with the monobutyl ether dried in 2 minutes, but before doing so it spread over the surface to such an extent that the marks were hopelessly blurred. On the other enamel the ink was still wet after 4 minutes, and it had not spread at all. Three minutes later it still had not dried, but had spread badly. From these results, and from the behavior of the two samples of lithographed and lacquered paper, it is evident that each material may be a special problem of itself. An ink may dry well on one material, but it may be of no value on another that looks like it. The few details given in this section merely point out the way for those who wish to experiment with special inks.

#### (c) INKS FOR GLASS AND PORCELAIN

Some of the inks recommended for writing on glass and porcelain contain sodium silicate solution, often called water glass, mixed with pigments that are not changed in color by the alkali in the silicate. Sodium silicate 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 cannot be removed completely by any ordinary means. In a typical formula for ink of this kind 11 parts of black drawing ink is mixed with 1 or 2 parts of the solution of sodium silicate.

The show-card inks made with a shellac-borax solution are fairly good for writing in glass, though the marks can be washed or rubbed off easily. The time-card ink described in a later section can also be used, but it is not a pleasant kind to write with.

The chemist must mark his porcelain crucibles for identification, and numerous substances have been employed for the purpose. One of the best, but the most expensive, is a solution of chloroplatinic acid ("platinum chloride"). When the writing is dry, the crucible is heated to redness to decompose the acid and leave a blackish deposit of platinum firmly attached to the glaze of the porcelain.

Dealers in artists' supplies sell paints for decorating china. They come in different colors, and when thinned a little by the addition of a drop or two of linseed oil, they are excellent for marking crucibles. The smallest tube of ink that can be bought holds enough for a great

deal of marking. A fine brush can be used, though a matchstick sharpened at the end serves the purpose well. The paint must be "burnt in" and the critical time is at the start of the heating, which must proceed slowly so as not to cause the oily mixture to spread. When the oil is burned off the crucible should be heated to redness.

A very simple ink is made by mixing two or three drops of a solution of sodium silicate ("water glass") with the same quantity of a pale-pink solution of cobalt chloride. When the liquids are mixed, the cobalt is precipitated as the silicate, in dark-blue gelatinous lumps. The lumps can be broken up and mixed through the liquid by means of the flattened end of a stirring rod. The marks are made with a brush or a pointed stick. They dry in a few minutes and are fired in the same way as the paint. There is no danger of their running, but at first they foam up as the water escapes from the plastic silicate. If the sodium silicate solution is colored to a moderately deep yellow by mixing with it a nearly saturated solution of potassium dichromate, the marks are green after firing, instead of blue, as when cobalt is used. The marks made in the way just described are somewhat rough on the surface, but they are very resistant and are not dissolved off by long digestion in a hot acid or alkaline solution.

#### (d) 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 after they have been tested. On application to the Bureau, a copy of the Letter Circular will be sent without charge. An old name for the mixture of barium sulfate and hydrofluoric acid which is described in the publication is "diamond ink," no doubt because it "cuts" glass, though not in the same way a diamond does.

#### (e) 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 black lines on the zinc. Labels written with this sort of ink have not been obliterated by continuous exposure to the weather for at least 10 years in the climate of Washington. Sometimes the writing becomes obscured by the products of the corrosion of the zinc, but rubbing off the whitish coating with the fingers restores the legibility.

It is interesting that unless there is enough rain to wash off the products of corrosion before they accumulate in quantity, the ink is not satisfactory. This is also the case in a greenhouse where the plants are sprayed at intervals, but with not enough water 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 dichromate. 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. The water has time to evaporate before it starts to corrode the zinc.

A simple formula for the ink is to dissolve 1 part each by weight of copper sulfate ("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. Because a similar reaction takes place with iron, 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 zinc 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.

#### (f) INK FOR BRASS

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

#### (g) INKS FOR OTHER METALS

The 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 are still better if ammonia water is added to the solution of silver nitrate. At first a black precipitate is formed, but a little 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 or friction, and may explode with great violence if roughly handled. 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.

#### (h) TIME-CARD INK

The hours at which mail is collected are sometimes written on white lacquered cards on the letter boxes. 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. This ink can be used for writing on a variety of materials and would no doubt be found satisfactory for garden labels not made of zinc.

The shellac varnish is made by dissolving 4 pounds of dry shellac in 1 gallon of alcohol, and these quantities will make a total volume of 1.4 gallons.

## (i) MEAT-BRANDING AND RELATED INKS

Ink for branding meats that are to be sold in interstate commerce come under the jurisdiction of the Bureau of Animal Industry, U. S. Department of Agriculture. The manufacturer must have each new supply of dye he buys tested and approved by that Bureau before he can legally make ink of it.

There are regulations concerning inks for printing or otherwise marking on wrappers which will come in contact with foods. The Food and Drug Administration should be consulted by those who may wish to make inks for food wrappers.

## IV. THE TESTING OF INKS

An essential part of each of the Federal specifications for inks is the section in which the methods of testing are described. If the specification gives the 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, and to show the bidder on a contract the minimum requirements of an ink that will be acceptable. By testing the sample and the standard side by side, any differences between the two become apparent at once.

The tests required in the Federal specifications are given in this section. On the last page of this circular the specifications are listed by symbol and name.

## 1. IRON GALLOTANNATE AND GALLATE INKS

The tests of iron gallotannate inks follow naturally from the definition of ink given by Schluttig and Neumann, and quoted on an earlier page. Their definition tells clearly 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 have a corrosion test. Iron gallate inks are tested in the same way as the gallotannate inks.

Because freshly made, well-settled ink should be clear, the first step in the examination of a sample is to allow it to remain undisturbed for 24 hours. If the sample is in several small bottles, which together make the pint of ink called for, their contents are poured into a single bottle 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. Sometimes the mixture of powder and water must be shaken frequently over a period of several hours so that all will be dissolved. In some cases the directions on the package advise the use of warm water. When dissolving the ferrous sulfate ink powder which is discussed on an earlier page, the last portions of gallic acid dissolve very slowly if the water is not warm. In any case, the bottle is not disturbed for 24 hours, so that any solid matter that may be in it can settle to the bottom. The bottle is then held up against the light and is slowly tilted away from the observer, who can thus easily see any sediment in the ink. There should be not more than traces of it. Very muddy ink can be rejected without making any tests.

If the ink passes this inspection, the test for keeping quality, the sediment test, is started next, because it takes 2 weeks to complete. In two similar clear glass vessels, for instance crystallizing glasses 50 mm (2 inches) in inside diameter and about 45 mm (1¾ inches) deep, are put 25-ml portions of the sample and of the standard. The dishes, loosely covered to keep out dust, are kept where they will be in diffused daylight, but never in direct sunlight, for 14 days. At the end of this time the sample should show no more surface skin than the standard, nor more deposit on the walls and bottom of the dish. In good iron gallate ink there should be not more than traces of sediment.

The sediment test is of considerable importance in these days when fountain pens are used by the majority of writers. This was not true when Schluttig and Neumann devised the test, but even in their day nobody enjoyed dipping his pen into a thick, muddy, and sometimes ropy, liquid in an ink bottle. For this test, and for the other comparative tests which follow, the standard ink should be in good condition. When a fresh batch of it is made, it should be put into bottles which hold no more than about 100 ml. These should be filled to the neck and then closed tightly with rubber stoppers.

The iron content of the sample ink is determined in a 10-ml portion, which is evaporated to dryness in an 8-cm evaporating dish on the steam bath. The organic matter is burned off, and the content of iron in the ash is determined by any suitable method. The fear is sometimes expressed that part of the iron may be lost as chloride volatilized at the start of the ignition, when burning off the organic matter. The Bureau has never found that this happens, but if the fear persists, all loss of iron in this way can be prevented by adding 2 drops of concentrated sulfuric acid to the ink before starting to evaporate it to dryness. This quantity of sulfuric acid is more than enough.

The amount of iron in 100 ml of copying and record ink should be not less than 0.58 g nor more than 0.70 g. For writing ink the limits are 0.29 and 0.35 g. Loosely, these quantities are sometimes called percentages (by weight, understood). Actually, they are slightly greater than the corresponding percentages, because 100 ml of ink weighs more than 100 g, which is the weight of the same volume of water.

Streaks of the standard and the sample ink are made side by side on a sheet of white bond paper of letter size. This is pinned to a small board or clamped to a pane of glass and held at an inclination of about 45°. The lower edge of the paper should overhang one-fourth to three-eighths inch, so that the ink will drip off instead of creeping between the back of the sheet and the support. It is desirable to arrange the paper so that the ink streaks will be made in the "machine direction," or lengthwise of the long band in which it comes from the paper-making 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 the two directions, one the machine direction and the other at right angles to it. If a piece of paper about an inch square is laid on water, in a few moments it will curl up on opposite edges, thus making a sort of trough. The axis of this trough is parallel to the machine direction of the paper. 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 ( $\frac{1}{8}$  inch) bore, and 250 mm (10 inches) long. A mark is etched or scratched 60 mm ( $2\frac{3}{8}$  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. The 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 touched to the upper edge of the sheet of paper, the finger is removed, and the ink is let flow out all at once and down across the paper. Two or three streaks of each ink are started about 1 inch apart. They may diverge widely or else run together near the lower edge of the sheet, but this makes no difference if strips suitable for the subsequent tests can be obtained. When all the streaks have been made, the sheet of paper is left in position until they are dry, and it is then put where it will be in diffused daylight, but not in direct sunlight.

It is not necessary, according to the specifications, 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 nearly equally fluid. It would be a waste of time to make an exact measurement. When the back of the paper is examined, the sample should show no more evidence of striking through than does 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 four strips, each about an inch wide, are cut from the lower end of the sheet, and crosswise of the streaks. One strip is soaked in distilled water for 24 hours, and the second strip is kept away from intense light and laboratory fumes. The third strip is soaked in a mixture of denatured alcohol and distilled water, in equal volumes, for 24 hours, and the fourth strip is kept in the dark for future comparison. Suitable pieces for the fading test are cut from the end of the sheet next to the fourth strip. These pieces are exposed at a distance of about 10 inches from a glass-enclosed carbon arc light for 48 hours.<sup>57</sup> When an arc lamp is not available, the test can be made by exposing portions of the streaks to direct sunlight, on the outside sill of a window that faces south, but at least double the number of hours will be required. In the three tests the sample should retain its color as well as does the standard. The comparison is made easier by the aid of the second and fourth strips, which were set aside.

Because of an optical effect, the fresh streaks are paler than writing done with the same ink. It is easy to see that the edges of the streaks are darker than the middle, because a slight excess of ink accumulates along the edges and dries there. The dark edges are narrow in comparison with the body of a streak, and they have little effect upon its depth of color as a whole. When a line made with a pen is examined with a lens it is seen to have dark edges, with a paler part between them. The greater part of the line, unless it is very wide, consists of

<sup>57</sup> A few of the Federal specifications in which fading tests are called for say that the commercial apparatus known as the "Fade-Ometer" shall be used. The holders for the samples are about 10 inches from the carbon electrodes.

the dark edges, so the whole line looks dark. The scratching of the paper by the two halves of the pen point must contribute to the extra blackness of the line, because paper absorbs more ink where it is roughened.

Because of the temptation for the manufacturer to increase the amount of free mineral acid in his ink, so as to delay oxidation and 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 in ink, and it is not likely that the other parts of the pen will be harmed by them. The millions of users of ordinary steel pens must be looked out for. It is incredible how many steel pens are sold each year. A recent year's supply for the Post Office Department alone was 5,673,-600 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. Needless to say, stainless-steel pens, which are but slightly dissolved by acids, should not be used for making this test.

Two new steel pens are taken for each of the samples under test, including the standard ink. They must be taken from the same box, in order to lessen the chance of there being some slight difference in composition that would affect the rate of attack by the acids. The pens are rinsed with alcohol, then with ether, and are dried in an air-oven at about 105° C (221° F). The two pens of each pair are weighed together to the nearest milligram. Because the washing with alcohol and ether is to remove the slight oily film from the pens, they should be handled with forceps. The next step is to immerse each pair of pens in 25 ml of ink, contained in a small flask or beaker. The pens should lie side by side, and not be "nested" together. After 48 hours the pens are removed from the ink, cleaned with water and by scrubbing to remove the clinging deposit, rinsed with alcohol, and dried at 105° C. They are now weighed, and if the loss in weight of the pair of pens in the sample is greater than the loss in the standard ink, the test must be repeated with both inks and with new pens, to check the first result.

Ink containing 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 upon the surface area of the pens. This would not be true if corrosion stopped as soon as all the free mineral acid was neutralized by dissolved iron. Rupert<sup>58</sup> 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 concentra-

<sup>58</sup> F. F. Rupert, *Ind. Eng. Chem.* 15, 489-493 (1923).

tion, 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 by another experiment in which gallic and tannic acids alone were used in the solution."

Rupert 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 but a crude one, and the results of duplicate determinations do not check one another very closely.<sup>59</sup>

As a rule, all parts of the pens seem to be equally attacked by the ink, but once in a while a strikingly different type of attack is met with. In this, the pen is dissolved 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 ( $\frac{1}{25}$  inch). This effect, which seems not to have been mentioned in print elsewhere than in earlier editions of this circular, is due to the ink, because both pens are always affected in the same way and to the same extent. The effect has never been noticed with the standard ink. A possible reason is that the ink contains an acid which is barely able to dissolve iron, so its action is limited to the parts of the pen that have undergone the most severe mechanical treatment, and have thereby been made more susceptible to attack by acids. This, of course, is where the metal has been cut.

Other ways of determining the acidity of inks have been suggested.<sup>60</sup> 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] cannot 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.

In the section on the aging of writing, the results of some experiments with alkaline paper are given. They indirectly confirm the statement just quoted.

So far as is known to the Bureau, all specifications for iron gallotannate ink require that the standard inks shall be made with hydrochloric acid, but tacitly permit the use of sulfuric acid in the ink bought. Apparently nobody has worked out and published any method for determining the amount of free hydrochloric or sulfuric acid in an ink of this type. The amount of chloride ion, sulfate ion, or both can be determined, but this must be done with due regard to the fact that the other ingredients of the ink may introduce complications.

<sup>59</sup> Mitchell, on page 180 of the book cited in footnote 1, says that the corrosion test is a somewhat crude method for determining the strong acids in inks. He describes an experiment in which a steel pen was immersed in 10 ml of ink and left there for a month. At the end of this time the pen had lost 5.18 percent in weight, and the ink was nearly solid. He cites several methods devised by other chemists for determining what he calls corrosive acids, but seems to prefer his own method, which consists in distilling a measured volume of the ink with sodium acetate, and titrating the acetic acid in the distillate. (See *Analyst*, **46**, 131 (1921).)

<sup>60</sup> Mitchell, already cited, and in *Analyst* **46**, 131 (1921). Schluttig and Neumann, p. 77-78. Rupert, already cited.



## 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 in that respect, because the manufacturer has little excuse for failing to make a clear solution of a dye. 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. This rarely happens.

Streaks are made on paper, and are subjected to the fading test, but for only 24 hours, instead of the 48 hours for blue-black inks. In red ink, pens corrode hardly more than they do in distilled water. In 48 hours the loss in weight will rarely be as much as 10 mg. A corrosion test is not required in Federal Specification TT-I-549.

Dye inks of other colors can be tested in the same way as red ink. Reasonable requirements are that the inks shall be clear, and that the streaks shall not fade nor be washed away completely.

## 3. STAMP-PAD INK

Stamp-pad inks dry almost entirely by soaking into the paper on which the impressions are made, because of the large proportion of glycerol they contain. It has already been explained that glycerol is practically nonvolatile at ordinary temperatures, and that it takes up water from humid air and loses at least part of the water in dry air. An important part of the testing required in Federal Specification TT-I-556 is based on these facts.

For making the tests, small stamp-pads are prepared by cutting disks of white felt about 6 mm ( $\frac{1}{4}$  inch) thick and 38 mm ( $1\frac{1}{2}$  inches) in diameter. The easiest way to cut them is with 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. The rings with the pads in them can rest upon a pane of glass, but it is neater and handier to solder disks of thin sheet brass to them, so as to make them into shallow boxes from which there can be no leakage of ink. Pads made in this way work quite as well as the more complicated arrangement described in the Federal specification. Equal volumes of the standard and of the sample ink are placed upon separate pads. Impressions are made with the 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. It is not required that the sample shall exactly match the standard in color, however. A part of each set of impressions must then be exposed at a distance of about 10 inches from the light of a glass-enclosed carbon-arc lamp for 24 hours, in the same way as when testing blue-black writing ink. The impressions made with the sample should fade no more than those made with the standard.

The inked pads are allowed to stand freely 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. This is determined by making more impressions, as well as by inspection.

As is evident, these tests can be used without change for testing both ordinary and quick-drying inks.

## 4. INDELIBLE MARKING INK FOR FABRICS

There is no formula for a standard ink in Federal Specification TT-I-542. The tests are intended to represent severe treatment in a laundry, and 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 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 instructions. If there are no instructions, the marking must be done according to the best judgment of the operator. 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 washings 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 bisulfite.*—Dissolve 5 g of sodium bisulfite 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 ("chloride of lime"), and dilute it to contain 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 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 bisulfite for 10 minutes, and the bleaching solution for 5 minutes. The marks must be clearly readable after the 24 washings.

## 5. BLACK AND COLORED DRAWING INKS

Federal Specification TT-I-528, for black waterproof drawing ink, and TT-I-531, for colored waterproof drawing ink, are largely based upon practical tests. There is no formula for a standard black ink. For the colored ink, standards are provided for seven colors. The inks supplied by the manufacturer need not match these exactly in shade, but must be at least equal to them in resistance to water.

Lines of different specified widths are drawn upon white drawing paper and upon tracing cloth. With the slit of the drawing pen set at an opening of 0.003 inch, it must be possible to draw with the black ink five lines, each 6 inches in length, at intervals of 5 minutes, "without extraneous assistance to promote the flow of ink." With the slit set at 0.012 inch, a set of lines is drawn, and then, before they are dry, a second set is drawn across them at right angles. The ink shall be regarded as unsatisfactory if the intersections of the lines are not clean and sharp. Other lines drawn with the slit at 0.012 inch are tested for smudging and blurring, by rubbing them with a dry fingertip 5 minutes after they are drawn. These lines are further tested by cutting the paper and tracing cloth 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 is 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 black ink shall not contain synthetic dyes. To test for them, mix 2 ml of the ink with 20 ml of alcohol to which five or six 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 have not more than a trace of color. A colorless filtrate is 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 sulfuric acid, and other reagents commonly used for the detection of dyes. Any change in 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.

Colored waterproof drawing inks are tested, in part, in comparison with inks made as described in the section on these inks. The seven "first choice" dyes are used for making these standard inks. Lines are drawn on drawing paper and on tracing cloth with the slit of the pen set to 0.003 and 0.02 inch. There must 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 its resistance to the growth of mold. The fastness of color when exposed for 12 hours at a distance of about 10 inches from a glass-enclosed carbon arc shall be determined.

## 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. Because many readers will prefer the 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 grams (g); and the unit of capacity is the liter, or 1,000 milliliters (ml), which is



the volume occupied by 1 kg of pure water at the temperature of its greatest density and under a pressure of 1 normal atmosphere. In many laboratories the milliliter is called a cubic centimeter.

For practical purposes at all ordinary temperatures, the weight of 1 liter of water can be taken as 1 kg, and of 1 ml of water as 1 g. So if a formula calls for 50 g of water, it will be accurate enough to take 50 ml.

If it is desired to measure other liquids than water, instead of weighing them, their specific gravities must be taken into account. For instance, if 35.4 g of concentrated sulfuric 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 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 density of the particles is not always the most important factor in the weight of a given bulk of them.

The conversion factors about to be given are based on accurate comparisons of the kilogram with the avoirdupois and apothecaries' pounds, and of the liter with 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 1 gallon of water is calculated from the factors for converting kilograms to pounds and gallons to liters, or  $2.2046 \times 3.7853$ , 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 1 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 "room temperature," as chemists often say when the exact temperature is of no importance, 8.33 avoirdupois pounds is sufficiently accurate.

The British, or imperial, gallon is 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 point cannot be ignored in making calculations, but when it comes to actually weighing or measuring the materials for making a liter of ink, even the first decimal figure may be of little importance. When making the standard ink of a Federal specification, it is advisable to weigh accurately to the second decimal place, if for no other reason than as a safeguard in case of a dispute. Lack of care in preparing the standard ink justifies doubt concerning the carefulness of the testing.

The way to use 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 1 liter. One gram equals 0.0353 avoirdupois ounce, and 1 liter equals 1.0567 quarts. Then, 1 g in 1 liter equals  $0.0353/1.0567=0.0334$  ounce in 1 quart;<sup>61</sup> and 5.5 g in 1 liter will be  $5.5 \times 0.0334=0.1837$  ounce in 1 quart. This last figure is multiplied by 4, which gives 0.7348 ounce in 1 gallon. Finally, 0.7348 is multiplied by 125 to get the weight of dye for 125 gallons. This is 91.85 avoirdupois ounces, and this divided by 16 gives 5.74 avoirdupois pounds of dye.

## 2. EQUIPMENT FOR MAKING INKS

The manufacturer of ink 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 that are furnished with the scales sold by dealers in photographic supplies are apothecaries', but metric weights can be obtained.

If ordinary bottles must be used instead of laboratory ware, and the solutions must be heated, there are two safe ways to go about it. One is to set the bottle in a deep vessel containing lukewarm water, and then to pour in hot water slowly, and not against the side of the bottle. While the hot water is being poured the bottle can be held by the neck and swirled around, to mix the cool and warm water more quickly. Some time must be allowed for the bottle and its contents to become warm, because there should not be too great a difference in temperature between the inside and outside of the bottle. Glass is a poor conductor of heat, and if the outside of the bottle expands from the heat, while the inside does not expand because it stays cold, strains will be set up that may break the bottle. Another way to heat a bottle of liquid is to set it in lukewarm water as before, but to put under it a spiral of heavy wire, or a piece of wire netting with the edges turned down, so as to raise the underside of the bottle at least one quarter inch above the bottom of the vessel. It can then be heated over a low flame or on a stove. The materials will dissolve more quickly if the bottle is swirled or shaken from time to time 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 so easily dissolved by many acids, and may also cause discoloration of some dyes.

## 3. DYES FOR MAKING INKS

Not all dyes are equally suitable for making inks, and in the formulas in this circular, various dyes have been suggested. In the formulas for the two standard blue-black inks the dye is given as "Soluble blue (C. I. 707; Sch. 539)." An explanation of the symbols in parenthesis 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 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 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 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 to it. Again, a manufacturer may sell a dye under two or more brand names. These names may indicate different degrees of dilution of the dye with colorless material.

<sup>61</sup> Those who prefer multiplication to division can start with the relation 1 quart=0.9463 liter. Then  $0.9463 \times 0.0353=0.0334$  ounce, as by the other way.

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 types to which they belong, and are further classified in each group according to their chemical formulas. The dyes are numbered serially, so any one number applies to only one dye. Thus No. 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) should be the most certain way of telling the seller exactly what kind of dye is wanted. In spite of this, it seems that not all dealers appreciate the advantages of the plan.

The Year Book of the American Association of Textile Chemists and Colorists gives the names by which the various dyes made in this country are called by the manufacturers. Usually there are several names for each dye, with the preferred one at the top of the list. In table 4 are the preferred names in the most recent edition of the yearbook. 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 not know what to buy. The Schultz numbers are not given, because they are no longer used in this country.

TABLE 4.—Dyes for various inks

RED DYES			
Name of dye	Colour Index number	Name of dye	Colour Index number
Amidonaphthol red <i>G</i> .....	31	Benzopurpurine <i>10B</i> .....	495
Azorubine.....	179	Fuchsin.....	677
Brilliant crocein <i>M</i> .....	252	Rhodamine <i>B</i> .....	749
Benzo fast scarlet.....	326	Erythrosine, yellowish.....	772
Congo red.....	370		
ORANGE DYES			
Crocein orange <i>G</i> .....	26	Toluylene orange <i>R</i> .....	446
Brilliant orange <i>R</i> .....	78	Toluylene orange <i>G</i> .....	478
Orange <i>R</i> .....	161	Pyrazol orange.....	653
Orange <i>TA</i> .....	374		
YELLOW DYES			
Naphthol yellow <i>S</i> .....	10	Auramine.....	655
Metanil yellow.....	138	Thiazol yellow.....	813
Brilliant yellow.....	364	Chloramine yellow.....	814
Tartrazine.....	640		
GREEN DYES			
Chloramine green <i>B</i> .....	589	Brilliant green.....	662
Diamine green <i>B</i> .....	593	Brilliant milling green <i>B</i> .....	667
Malachite green.....	657	Light green <i>SF</i> , yellowish.....	670
BLUE DYES			
Naphthol blue-black.....	246	Soluble blue.....	707
Benzo cyanine <i>R</i> .....	405	Xylene cyanole <i>FF</i> .....	715
Benzo blue <i>BB</i> .....	406	Victoria blue <i>B</i> .....	729
Diamine sky blue <i>FF</i> .....	518	Wool blue <i>G</i> , extra.....	736
Benzo sky blue.....	520	Methylene blue.....	922
Bavarian blue <i>DSF</i> .....	705	New methylene blue <i>N</i> .....	927
Methyl cotton blue.....	706	Indigotin <i>IA</i> (indigo).....	1, 180
VIOLET DYES			
Diamine violet <i>N</i> .....	294	Methyl violet <i>B</i> .....	680
Oxamine blue <i>4R</i> .....	471	Crystal violet.....	681
Hofmann's violet.....	679	Formyl violet <i>S4B</i> .....	698



TABLE 4.—*Dyes for various inks*—Continued

## BROWN DYES

Name of dye	Colour Index number	Name of dye	Colour Index number
Bismarck brown <i>R</i> .....	332	Benzo brown <i>G</i> .....	606
Benzamine brown <i>3GO</i> .....	596		

## BLACK DYES

Sulfon cyanine black <i>B</i> .....	307	Nigrosine, spirit-soluble.....	864
Columbia fast black <i>FF</i> , extra.....	539	Nigrosine, water-soluble.....	865
Direct deep black <i>RW</i> , extra.....	582		

In the two Federal specifications for blue-black inks, the dye that must be used in the standard inks is the particular soluble blue designated as C. 1. 707. According to the Colour Index, this dye is derived from a mixture of triphenyl-pararosaniline and diphenylrosaniline. These two dyes are insoluble in water, but dissolve easily when converted into the trisulfonic acids, or some of their salts. Because the sulfonation is never complete, the dye always contains some of the disulfonic, or even of the monosulfonic, acid. The acids are not used as such, but are converted into their sodium, ammonium, or calcium salts. Schluttig and Neumann used bavarian blue *DSF*, which is chiefly the sodium salt of the disulfonic acid. It is said that much of the dye sold as soluble blue for ink is not derived from pararosaniline, but from its methyl derivative, rosaniline. In table 4 this rosaniline dye is listed as methyl cotton blue.

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 fabrics. Because of the composition of iron gallotannate and gallate 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 dye is not sulfonated as completely as it should be, it is advisable when buying to specify that the dye must be "for ink." A reliable dealer will not then supply soluble blue that is satisfactory for ordinary uses, but not for making ink. The iron gallate inks require exceptionally good dye, and there may be some difficulty in getting it. Unfortunately there are no laboratory tests, aside from making a small batch of ink and testing it, by which it can be determined whether the dye is of the desired quality. With suitable dye, the iron gallate inks show greater stability in the sediment test than the iron gallotannate inks.

A few dyes that are more or less satisfactory substitutes for soluble blue are naphthol blue-black, benzo blue *BB*, diamine sky blue *FF*, and benzo sky blue. Acid black *N*, when used at the rate of 3.5 g in a liter, has nearly the same shade of color as soluble blue. These dyes have not been tested by this Bureau in iron gallate inks. 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*." Their green dye was guinea green *B*, called by them 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 paint 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 colorless substance to dilute them to the strengths to which the dyers have long been accustomed, because the formulas furnished by the manufacturers are based upon these diluted dyes. This is a recognized trade practice, not 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 can be found formulas, methods of testing, and references to still other books and to articles that have appeared in scientific and technical journals. There is no dearth of reading matter on 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, Pa., 1927).
2. H. Bennett, *Practical Everyday Chemistry* (Chemical Publishing Co., New York, N. Y., 1934).
3. H. Bennett, *The Chemical Formulary*, 4 vol. (vols. 1 and 4, Chemical Publishing Co., New York, N. Y., 1933 and 1939; vols. 2 and 3, D. Van Nostrand Co., New York, N. Y., 1935 and 1936).
4. W. T. Brannt and W. H. Wahl, *Techno-Chemical Receipt Book* (H. C. Baird & Co., Philadelphia, Pa., 1905).
5. D. Carvalho, *Forty Centuries of Ink* (Banks Law Publishing Co., New York, N. Y., 1904).
6. W. B. Gamble, *Chemistry and Manufacture of Writing and Printing Inks* reprinted from *Bul. New York Public Library* 29, 579, 625, 706 (1925). (Bibliographic, with references to many United States and foreign patents).
7. *Henley's Twentieth Century Book of Recipes, Formulas and Processes* (Norman W. Henley Publishing Co., New York, N. Y., 1928).
8. *Jameson's Manufacturers Practical Recipes* (Lewis Jameson & Co., Ltd., London, England, 1929).
9. J. B. Lavay, *Disputed Handwriting* (Harvard Book Co., Cambridge, Mass., 1909).
10. S. Lehner, *Manufacture of Inks* (translated, with additions, by W. T. Brannt. H. C. Baird & Co., Philadelphia, Pa., 1892).
11. C. A. Mitchell, *Inks, Their Composition and Manufacture*, 4th ed. (J. B. Lippincott Co., Philadelphia, Pa., and New York, N. Y., 1937).
12. A. S. Osborn, *Questioned Documents* (Lawyer's Cooperative Publishing Co., Rochester, N. Y., 1910).
13. J. H. Oyster, *Spatula Ink Formulary* (Spatula Publishing Co., Boston, Mass., 1912).
14. O. Schluttig and G. S. Neumann, *Die Eisengallustinten* (The Iron-Gall Inks) (v. Zahn & Jaensch, Dresden, Germany, 1890).
15. *Scientific American Cyclopedia of Formulas*, edited by A. A. Hopkins (Munn & Co., New York, N. Y., 1921).
16. E. Spon, *Workshop Receipts* (E. & F. N. Spon, London, England, and New York, N. Y., 1917).
17. N. Underwood and T. V. Sullivan, *Chemistry and Technology of Printing Inks* (D. Van Nostrand Co., New York, N. Y., 1915).
18. F. B. Wiborg, *Printing Ink* (Harper & Bros., New York, N. Y., 1925).
19. H. J. Wolfe, *Manufacture of Printing and Lithographic Inks* (MacNair-Dorland Co., New York, N. Y., 1938).
20. Carleton Ellis, *Printing Inks* (Reinhold Publishing Corp., New York, N. Y., 1940).

A few 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 were formerly issued as circulars of the Bureau, under the general title, United States Government Master Specifications. These circulars have long been out of print, and the specifications are now parts of the Federal Standard Stock Catalog, and are sold by the Superintendent of Documents. They are listed further on. In congressional districts throughout the country Congress has designated many libraries as Government depository libraries. They are entitled to receive all Government publications they care to have, with the understanding that the publications shall be available for consultation by the general public. Other libraries, though not Government depositories, have more or less complete series of the publications. Because libraries borrow books from one another, the Government publications are more accessible than they would otherwise be.

Government publications which are in print can be bought from the Superintendent of Documents, United States Government Printing Office, Washington, D. C. Payment should not be made in postage stamps, and money is sent at the buyer's risk. Postal money orders, express orders, New York drafts, and coupons sold by the Superintendent of Documents at \$1 for 20 are accepted. The coupons are good until used. Publications are sent under frank to all parts of the United States and its possessions, and to countries that extend the franking privilege. Buyers in other countries should add to their remittances about one-third of the price of the publications to cover postage. When ordering, the name of the issuing Bureau as well as the title and number of the publication should be given. Time is lost if orders are sent to the Bureaus concerned.

Copies of United States patents can be bought for 10 cents apiece. They should be ordered from the U. S. Patent Office, Washington, D. C.

The following Government publications relate to inks:

J. B. Tuttle and W. H. Smith, *Analysis of Printing Inks*, BS Tech. Pap. T39 (1915). (Out of print.)

*Composition, Properties and Testing of Printing Inks*, BS Cir. C53 (1915). (Out of print.)

*Inks—Their Composition, Manufacture, and Methods of Testing*, BS Cir. C95, 1st ed. (1920). (Out of print.)

*Inks, Typewriter Ribbons, and Carbon Paper*, BS Cir. C95, 2d ed. (1925). (Out of print.)

*Inks*, BS Cir. C400 (1933). (Out of print.)

*Inks*, Cir. NBS C413 (1936). (Superseded by the present circular.)

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). (Out of print.) The methods differ considerably from those of the Federal specifications.

A. E. Kimberly and B. W. Scribner, *Summary Report of National Bureau of Standards Research on Preservation of Records*, Misc. Pub. NBS M154 (1937). 10c.

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.

C. E. Waters, *Quick-drying stamp-pad inks*, J. Research NBS **20**, 543-547 (1938). RP1087. 5c.

*Dry Etching of Glass*, BS Letter Circular LC150. Free on application to this Bureau.

*Carbon Paper and Typewriter Ribbons*, Letter Circular NBS LC597. Free on application to this Bureau.

*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, May 10, 1940.





