

DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 95

INKS—THEIR COMPOSITION, MANUFACTURE, AND METHODS OF TESTING

{1st Edition}

JUNE 28, 1920



PRICE, 5 CENTS

Sold only by the Superintendent of Documents; Government Printing Office,
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I. INTRODUCTION

This circular contains a discussion of the composition and manufacture of inks and the analytical procedures used in their examination.

The methods as set forth in this circular are not original, but have been compiled from a variety of sources, and modifications have been introduced when necessary.

The methods are presented in this form because of their inaccessibility, heretofore being scattered throughout chemical literature. They have been selected from the mass of material on the subject and have been tested and found to be satisfactory.

II. HISTORICAL

The earliest use of liquid which can be described as ink is found among the archeological treasures of Egypt, dating back to 2500 B. C. This ink was black in color. The basis for the black inks used on papyri was undoubtedly carbon, a substance which has the advantage of being easily procurable, while at the same time it is indestructible except by fire. The ink was probably prepared from vegetable or animal charcoal mixed with gum, oil, or varnish.

Chinese or Indian ink was made as far back as 2697 B. C. by Tien-Tchen. Its base like that of the Egyptian inks, is carbon.

There was a time not so far back in history when the act of writing was a polite accomplishment known to only a privileged few. Then the commercial manufacturer did not exist, ink making was considered a great accomplishment, and family receipt books were handed down through generations as a precious bequest. In 1571 a book was written by John de Beau Chesne entitled "A Book Containing Divers Sorts of Hands." This book contains "Rules made by E. B. for his children to learne to write bye." They include directions for making ink and are quaint enough to deserve quotation:

To make common yncke of wyne take a quarte,
Two ounces of gomme, let that be a parte,
Five ounces of galles, of copres take three,
Long standing doath make it better to be,
If wyne ye do want, ragne water is best,
And as much stuffe as above at the least:
If yncke be too thick, put vinegre in,
For water doath make the colour more dim.
In hast for a shift when ye have a gread nede,
Take woll, or wollen to stend you insteede,
Whiche burnt in the fire the powder bette small
With vinegre, or water make yncke well all.
If yncke ye desire to keep long in store,
Put bay salte therein, and it will not hoare.
If that common yncke be not to your minde,
Some lampblack thereto with gomme water grinde.

The transition from carbon inks to inks made from galls and iron was very gradual. The earliest scientific investigation of the chemical reactions between iron salts and an infusion of galls appears to be that of Robert Boyle. He showed that a precipitate was obtained by mixing these ingredients of ink. The use of dyestuffs, such as logwood or indigo, to strengthen the color of the ink was practiced to a small extent in the eighteenth century.

The next development in the manufacture of ink is found in the use of aniline dyes, not merely for coloring writing fluids, but also for taking the place of indigo in the black inks. The subject was taken up by the Prussian Government in 1879, and aniline inks were discarded for documentary writing because of their lack of permanence.

Several different countries have adopted ink regulations. All inks used for official purposes in Massachusetts conform to the formula given later in this circular. Subsequently the U. S. Government adopted the same specification as Massachusetts for the standard writing ink used in all Government offices.

III. COMPOSITION AND MANUFACTURE OF INKS

Writing ink is a solution or fine suspension in water of some colored substance which will leave a permanent mark upon paper after drying. It is judged by its permanence, durability, and writing qualities. By permanence is meant the resistance which the writing will show to the agents of time such as light, moisture, and moderate heat. The durability is judged by the freedom from the formation of scum, sediment, and mold. The writing quality is a factor which must also be taken into consideration, inasmuch as some fluids, in spite of excellent durability and permanence, are unsuited for pen work because of improper consistency, high acidity, or insufficient color.

1. CARBON INKS

Inks having carbon or a carbonaceous compound in a finely divided state for their pigment date back to periods of remote antiquity, though for writing purposes they have to a large extent been superseded by inks in which the coloring matter is more or less in solution.

Sepia, a black secretion of the common cuttle-fish, was used by the Romans for writing purposes. Now, however, it is used almost exclusively in the manufacture of "sepia" for artists. The ink sacs are pulverized, and the powder is triturated with caustic soda and boiled for 20 minutes. The liquid is then filtered, neutralized with hydrochloric acid, and the precipitated pigment repeatedly washed with water and dried at a low temperature. The pigment is ground to a fine powder and made up into cakes.

Indian or Chinese ink is made from carbon and suitable materials. When carbonaceous products, such as oil, resins, or tar, are burned with an insufficient supply of air, carbon is formed. This material, known as lampblack, is further purified by heating to redness in a closed crucible. The Chinese burn various substances for their lampblack, among them rice straw, pine wood, and vegetable oils. The most important of the vegetable oils is tung oil, which yields a brilliant black ink.

Indian ink is made from a mixture of glue and lampblack. These materials are heated together, cooled, and camphor or some such preservative is added. The mixture is then pressed into cakes and sold as a commercial product.

Modern carbonaceous inks are made from mixtures of gum arabic, shellac, and borax, with carbon in suspension.

2. GALLOTANNATE OF IRON WRITING INKS

Ordinary writing ink consists essentially of an aqueous solution of iron gallotannate, although Prussian blue, chrome logwood, copper logwood, and dye solutions are sometimes used. For ordinary work the iron gallotannate has been found to be the most satisfactory. This is the type of ink that has been adopted by the Government. The galls used in the ink are found on branches, shoots, and leaves of trees. They are produced by insects, the best known being the gallwasp. The galls contain tannin, gallic acid, ellagic and luteogallic acids, chlorophyll, gum, starch, sugar, proteid, potassium salts, and water.

The galls are soaked in water and the extract is used in ink making. The most important substance extracted is a tannin which is given the name of gallotannic acid to distinguish it from other tannins. Tannins vary greatly; they are described as iron bluing or iron greening, according to the color of the precipitate they form with iron salts.

This difference is evidently one of constitution, for one group of tannins can be converted into gallic acid and yield pyrogallol, while the other group does not give these reactions. Only the iron-bluing tannins are suitable substances for the manufacture of black ink, as has been shown by Schluttig and Neumann,¹ who found that mixtures of various tannin extracts with solutions of iron salts gave bright green colorations on paper, but that after six months' exposure only rust-like stains were left. Tannins are extracted from other sources than galls. Chestnut bark is a source of tannin, which, however, is not as satisfactory for ink making as the tannin made from an infusion of nut galls. Other sources are: Sumac, divi-divi—the name given in commerce to the dried pods of a South American shrub, myrobalans—the fruit of different species of *Terminilia* growing in India, valonia, acorn cups, and oak bark. All of these materials, with the exception of the last named, produce iron-bluing tannins. Iron salts are of primary importance in ink making, because they form insoluble, permanent compounds with tannins and produce a black color. The addition of an acid is necessary to prevent precipitation and to keep the iron in solution. For this purpose sulphuric or hydrochloric acid is used. The Government has adopted the following specifications for inks: The ink must be a gallotannate of iron ink, not inferior in any essential quality to one properly prepared after the following formula:

¹ Die eisengallustinten, p. 38.

	Grams
Tannic acid.....	23.4
Gallic acid.....	7.7
Ferrous sulphate.....	30
Dilute hydrochloric acid, U. S. P.....	25
Phenol.....	1
Suitable blue dye.....	2.2
Water to make a volume of 1000 cc at 15.6° C.	

3. LOGWOOD AND DYESTUFF INKS

In the manufacture of inks where permanence is not a necessary factor many dyes in aqueous solutions are used. For ordinary writing purposes these inks are very satisfactory, because they do not contain acid and have no corrosive effect on pens. A material commonly used for inks is logwood. The logwood is digested with hot water, and the extract obtained is used for coloring. By adding a very small proportion of potassium chromate to a decoction of logwood a deep-black fluid is obtained which can be used as an ink without further treatment. Copper-logwood inks are made by boiling alum, copper sulphate, and logwood with water and filtering the solution. The filtrate is a red-violet ink, which writes pure violet, then rapidly darkens.

4. INK TABLETS AND POWDERS

Ink tablets and powders, as their names imply, are designed to produce ink by being dissolved in water. To be entirely satisfactory the solution formed must possess all the properties of a high-grade writing fluid. As stated before, most inks belong to the iron-tannin class.

Several years ago the attention of this Bureau was directed to ink powders by one of the departmental supply divisions. It was found that these powders contained organic dye, but none of the other ingredients necessary for permanent records. The records produced by these inks were fugitive to sunlight and could easily be washed out with water. It was obvious, therefore, that a suitable ink-powder would have to contain the important ingredients of writing fluid, namely, tannic acid and ferrous sulphate.

All of the materials used in the manufacture of ink are solid, with the exception of hydrochloric acid, and it is necessary that this acid or some similar material be present in order to prevent the iron from precipitating. Experiments have shown that certain solid substances of an acid character can be used in the place of hydrochloric acid. Failure to use such material will result in a powder which, when dissolved in water, will have a

tendency to form a thick scum or sediment after standing a few days. A few manufacturers have thought that the dried and ground residue from ordinary ink could be used. As might be expected, the hydrochloric acid escapes with the water on evaporation, and, furthermore, the iron-tannin compound is largely rendered insoluble by the process.

The results of experiments seem to indicate that organic acids or acid salts of mineral acids, in proper amounts, may be used as a substitute for hydrochloric acid.

The advantages that would accrue from the use of powders and tablets are many. A quart bottle of ink ready for shipment weighs about 5 pounds and occupies about 275 cubic inches, whereas the quantity of powder sufficient to make a quart weighs approximately 2 ounces and occupies only 8 cubic inches. Another important factor is the great reduction of loss by breakage, which entails loss of the ink and which may ruin other articles which come in contact with the fluid. The danger of freezing is entirely eliminated. Another point that is worthy of consideration is the superior keeping quality of a powder over a liquid.

There are a few objections to the use of ink powders: (1) The production of this material is still in the experimental stage; (2) the user must furnish his own container; (3) careless persons may not make up the ink properly; and (4) the water in certain localities may contain ingredients which are deleterious to the ink.

5. COPYING INKS

Most writing inks are capable of yielding one or more copies when pressed with suitable moist paper soon after writing. Thus an ordinary iron-gall ink will give a faint copy before it has become completely oxidized, but when once the coloring matter becomes completely insoluble, copies can no longer be taken. As the process of copying tends to make the original writing too faint, it is necessary to have an additional quantity of coloring matter in the ink, together with a certain proportion of gum or other adhesive material to attach this excess of coloring matter to the surface of the paper and to protect it from too rapid oxidation. Dextrin is sometimes employed in place of gum. Sugar, too, is frequently added for the same purpose; however, it leaves the writing more or less sticky and is, therefore, objectionable. A small amount of glycerol is a common constituent of copying ink, its object being to prevent the gum from completely drying.

If, however, it is added in too large an excess, the ink will smudge. Generally speaking, iron gall and logwood copying inks should contain from 30 to 40 per cent less water than inks of the same formula intended for use as writing inks only. Below is the formula, adopted by the Government, to which all copying inks must conform:

	Grams
Tannic acid.....	46.8
Gallic acid.....	15.4
Ferrous sulphate.....	60.0
Gum arabic.....	10.0
Dilute hydrochloric acid U. S. P.....	50.0
Phenol.....	1.0
Suitable blue dye.....	4.4
Water to make a volume of 1000 cc at 15.6° C	

6. MARKING INKS

Long ago it was found that certain plants exude juices which yield colors of great durability, particularly on linen; hence the Chinese and the natives of India used these juices for marking linen. Many tropical trees, such as the *Semecarpus anacardium* and the cashew nut, produce fruits the juices of which have long been known as "marking" inks.

Many attempts have been made to study the effect of certain juices on linen and their resistance to washings. In 1904 a new industry was started in Mexico, the pulp of the *Escleloahnitl* being then first made into marking ink on a commercial scale.

Of the different substances that have been employed as marking inks the best known and most commonly used has been a solution of a silver salt, the reduction of which in the fibers of the material leaves an insoluble black deposit of a more or less permanent nature. The earliest ink of this type required the linen to be previously treated with what is known as a ponce and then dried, but these inks have now been entirely superseded by others which are reduced by passing a hot iron over the writing.

Marking inks have been made in innumerable ways. One silver marking ink contained water, platinum, silver, tartaric acid, ammonia, gum, and a pigment.

Marking inks may contain salts of metals, such as gold and platinum, which are too expensive for general use; also the sulphides of heavy metals, such as iron, zinc, and copper, or organic substances, such as nonvolatile fats, in the presence of a suitable metallic hydroxide or sulphide. Aniline marking inks are also made. They consist of two solutions which are kept separate

until just before use. The writing done with this ink is not removed by water, but is not very resistant to the action of alkalis. Many patents have been secured for marking inks; among them are "Dimitry's bichromate marking ink," which consists of a soluble coloring matter mixed with gelatin and potassium dichromate, and "molybdc marking ink," prepared by dissolving molybdc oxide in hydrochloric acid and adding gum arabic, sweet wood extract, and water. When the writing was dry the linen was treated with a solution of tin chloride.

Many marking inks manufactured at present consist chiefly of cresol and dye.

7. CANCELING INKS

The demand for these inks has come almost entirely from Government departments or from manufacturers who pay the tax on the articles which they produce and, consequently, must cancel the revenue stamps furnished them. The ink must contain pigment and dyes and must penetrate the fiber of the paper of the envelopes and stamps to such an extent that the mark can not be removed by erasure or washing without defacing the stamps sufficiently to prevent their use a second time. The inks are quite varied in composition. Lampblack is used as a pigment with the addition of a coal-tar dye; the liquid used as a base for the ink consists of a nondrying oil.

8. STAMPING INKS

The ink used for rubber stamps should be such that, when applied to a suitable pad, it remains sufficiently fluid to adhere to the stamps. At the same time the fluidity should cease by the time the stamp is pressed upon an absorbing surface such as paper. Formerly these inks were made by rubbing up pigments in fat to a paste. Now, since most stamping inks are made from glycerol and coal-tar dyes, the manufacture is quite simple. The dye, such as fuchsine, methyl violet, water blue, emerald green, etc., is put into a dish and glycerol poured over it; the mixture is then heated to about 212° F. The coal-tar dyes used must necessarily be soluble in hot glycerol.

9. DUPLICATING INKS

These inks consist of a mixture of pigment and oil, though rosin soaps in small quantities are sometimes found. Of the pigments the most important is carbon. The iron blues are used to a large extent with the carbon; these are mixtures of ferricyanides and

ferrocyanides of iron and potassium. The best known of these pigments is Prussian blue, obtained by adding a ferric salt to potassium ferrocyanide. Ultramarine is used to some extent. The true ultramarine is the mineral lapis lazuli. This is too rare to use. What is commonly known as ultramarine is the artificially prepared pigment, made by heating together china clay, soda, sulphur, and charcoal. The oil fraction may contain castor oil, sulphonated castor oil, rosin oil, cotton-seed oil, sulphonated cotton-seed oil, and mineral oil. The determination of the total amount of the oil present is a matter of too much difficulty to justify the time required. Determining the various constants, such as iodine number, saponification number, acid number, etc., does not give very reliable data regarding the composition.

10. SYMPATHETIC INKS

The term sympathetic ink is applied to writing fluids which yield characters that remain invisible until heated or treated with some suitable reagent. Such inks appear to have been known in the early days of the Roman Empire, for Ovid mentions milk as a suitable liquid, while Pliny refers to the juices of different plants.

In 1715 Waiz discovered the use of solutions of cobalt salts as sympathetic inks, and the French chemist Hellot also gave a description of them a few years later.

Battista Porta (1567) described various kinds of invisible inks such as, for example, a solution of iron sulphate. The writing was made visible by sponging with a decoction of galls. He also alluded to a colorless ink which was made visible by dusting the paper with a certain black powder.

Lemery (1720) described sympathetic inks which appear to consist of lead acetate, the writing being made visible by the application of a sulphide.

IV. ANALYTICAL PROCEDURES

The purpose of the analysis is to ascertain the approximate composition of the inks. In the case of inks having an oil base it is not necessary that the analysis should be of the highest accuracy, and in many cases this is impossible for the various mixtures of oils and dyes. Practical tests are, in these cases, the most reliable, inasmuch as they give a direct indication as to the suitability of the ink for the purpose for which it was designed.

With writing inks one of the most important tests is their resistance to light and reagents, for the number of substances entering into the composition of the ink is so large that their influence on the permanency of the writing is uncertain, hence the necessity for practical as well as chemical tests.

1. ANALYSIS OF WRITING INKS

These inks may be divided into two classes: (1) The iron-tannin inks, and (2) the logwood and dyestuff inks. The determinations of an analytical character which are of value are as follows:

(a) TOTAL SOLIDS.—Evaporate 10 g of ink to dryness in a porcelain dish on the steam bath, heat in an oven at 105° C for one hour, cool in a desiccator, and weigh.

(b) ASH.—Burn the residue from the determination of total solids at the temperature of low redness. Cool in a desiccator and weigh.

(c) IRON.—Add about 25 cc of concentrated hydrochloric acid to the porcelain dish containing the ash and heat on the steam bath until the material is dissolved. If the ash has not been ignited at too high a temperature, the iron oxide will dissolve in about 15 minutes on the steam bath. Dilute to 400 cc, filter, heat to boiling, add ammonium hydroxide until the solution is ammoniacal, and boil until the precipitate agglomerates. Filter, wash with hot water, ignite in a weighed crucible, cool, and weigh.

(d) SULPHURIC ANHYDRIDE.—To 10 g of ink in a fused silica dish, add 10 cc of 10 per cent sodium-carbonate solution. Evaporate to dryness on the steam bath, and heat for one hour in an oven at 120° C. Ignite and cool, then place the dish in a 600 cc beaker, cover with distilled water, and heat for one hour on the steam bath. Filter, add 5 cc of bromine water to the filtrate, and heat for one-half hour on the steam bath to oxidize to sulphate any lower sulphur compounds which may have been formed in the ignition. Render slightly acid with hydrochloric acid, add 10 cc of 10 per cent barium-chloride solution, and let stand overnight. Filter, wash, ignite, and weigh.

(e) TANNIN.—Place 10 g of ink in a Kempf's extraction apparatus, add 10 cc of concentrated hydrochloric acid, and dilute with water to about 2 inches below the overflow tube. Fill the bulb with ethyl acetate and extract continuously until the tannin is all removed by the ethyl acetate. This will require about two hours. Remove the ethereal solution and shake it out two or

three times with a half-saturated solution of potassium chloride to remove any iron salts present. Evaporate the ethereal solution in a vacuum, take up the residue with a little water, filter if necessary, evaporate in a tared dish, dry at 105° C in an oven, and weigh.

(f) DYE.—As a rule it is unnecessary to determine the dye which has been used, but if this is desired, the dyes should be separated into groups according to their constitution, and then subdivided by their behavior with separate reagents.

Prussian blue may be determined qualitatively by adding sodium hydroxide to the ink, filtering, and acidifying with hydrochloric acid. The addition of ferric chloride gives a deep blue color if Prussian blue is present.

Logwood in ink is readily identified by the color changing to bright red on the addition of hydrochloric acid.

Ultramarine.—Add a few drops of hydrochloric acid to the ash. If ultramarine is present, a strong smell of hydrogen sulphide will be noticed. The ash also possesses a characteristic blue color.

(g) CHROMIUM.—In cases where logwood is found in inks, chromium is usually also present. Remove the ash to a platinum crucible, add 10 g of sodium carbonate, fuse in an oxidizing atmosphere until there are no further unattacked particles in the melt, take up the melt in water, filter, acidify with acetic acid, heat to boiling, add 10 per cent barium chloride solution, and let stand. A yellow precipitate indicates the presence of chromium. Filter off the barium chromate through a weighed Gooch crucible, ignite gently, cool, weigh, and calculate Cr_2O_3 .

(h) SPECIFIC GRAVITY.—Determine the specific gravity at 15.6° C and refer to water at the same temperature.

(i) ACTION ON PENS.—Clean a pen with alcohol and ether, dry, and weigh. Immerse this in a small vial containing 20 cc of ink and let stand for 24 hours. At the end of this time remove the pen, clean with alcohol and ether, note whether or not the metal appears to be corroded, and whether the ink has become thick. Weigh the pen and record the loss in weight.

(j) STREAK TESTS.—The sample should be allowed to stand 24 hours so that any sediment which has been shaken up in handling may settle. The streak tests should be made before the chemical analysis is started. In this way the ink will have an opportunity to oxidize in the fibers of the paper while the chemical analysis is being performed, and time will be saved. The streaks are made on

all-rag writing paper of good quality, 11 by $5\frac{3}{4}$ inches. The paper is held by means of clamps over a glass plate 8 inches wide, at an angle of 45° , and the ink is allowed to run over the paper from pipettes holding about 0.6 cc of ink. The pipettes are made from glass tubing having a 3.5 mm bore and length of about 250 mm, with a mark 62 mm from the lower end. By drawing the ink up to the mark and holding the pipette vertically against the paper near the top and allowing the ink to flow suddenly down the paper, uniform streaks will be obtained.

(k) PENETRATION AND FLUIDITY.—The ink should penetrate into the fibers of the paper, but should not pass through it. This can be best observed on the streaks made for exposure tests. Stickiness should also be observed, and by carefully making the streaks, a very good idea of the fluidity can be formed. A normal ink should give an oval head to the streaks, and the rest should be nearly uniform in width; a very fluid ink gives a wide head and the streak rapidly narrows down.

(l) KEEPING QUALITY.—It is very important to determine whether an ink will keep or not. Some samples will show very little decomposition at the end of a year, while others deposit so much sediment and form so much scum at the end of a week that they can not be used. Place a quantity of ink in a bottle and cork it tightly. Place the bottle in diffused sunlight and note the ink from day to day. Observe the amount of sediment and scum.

(m) RESISTANCE TO LIGHT AND REAGENTS.—After the ink has oxidized completely in the fibers of the paper (this will require at least five days and in most cases seven or eight), cut the streaks into strips. Beginning at the top, make the first strip 3 inches wide and then cut three more strips 2 inches wide. Place the ink number and strip number on the back of each in pencil. Place strip No. 2 in a dish of water at room temperature and strip No. 3 under the ultra-violet light for 48 hours. (When the ultra-violet light is not available, the strips should be placed in the sunlight; however, in that event they should be allowed to remain at least one week.) Strips No. 1 and No. 4 are to be kept in the dark.

Strip No. 4 may be cut into small pieces and various other reagents may be employed, such as 95 per cent alcohol; 90 volumes of water and 10 volumes of ammonium hydroxide; 2 per cent hydrochloric acid; 2 per cent sodium hydroxide; and bleaching powder solution containing N/200 available chlorine. The tests used are relative and it is well to have a standard ink (formula given on p. 8) for comparison.

2. ANALYSIS OF INK POWDERS AND TABLETS

(a) **MOISTURE IN POWDER.**—Weigh one-half gram of the powder in a tared evaporating dish. Heat in an oven at 105° C for two hours, cool in a desiccator and weigh.

(b) **CALCULATED SOLIDS.**—Calculate the solids which the ink would possess if the powder dissolved completely in the specified volume of water.

(c) **TOTAL SOLIDS.**—Prepare 8 ounces of the ink from the powder, being careful to make it up according to directions. Let stand for 24 hours and then analyze for total solids as given under foregoing section “(a) Total Solids.”

(d) **ASH, ETC.**—The analysis of the ash, iron, sulphuric anhydride, and tannin, the calculation of specific gravity, and the physical tests are conducted as under foregoing section “1. Analysis of Writing Inks.”

3. ANALYSIS OF COPYING INKS

The same tests are applied to copying inks that are discussed under “1. Analysis of Writing Inks;” however, when possible, the inks should be tested for adhesives.

(a) **GUM AND DEXTRIN.**—The test for the presence of gum and dextrin is very unsatisfactory and thus far no definite method for their detection can be given. The fact that in a good many cases the dye can not be removed makes the analysis impracticable.

(b) **GLYCEROL.**—The total solids of the ink are treated with alcohol, the alcoholic extract is evaporated, and the residue tested for glycerol. Glycerol gives off fumes of acrolein when heated with potassium bisulphate.

(c) **COPYING TEST.**—Write a few lines on a sheet of paper with the ink under examination, place the paper in the copy book and allow it to remain in the press for one minute. Remove and allow it to dry. Portions of the original writing and of the copy should be exposed to the ultra-violet light and tested with reagents as prescribed for writing inks.

4. ANALYSIS OF MARKING INKS

The composition of a marking ink is of subsidiary importance as compared with the result of practical tests. The chief requirements of a good marking ink are: (1) It must not injure the fibers of a fabric; (2) it must not be too viscous to flow smoothly from the pen, nor yet so fluid as to “run” when applied to linen; (3) it must produce characters which rapidly darken when treated

with a moderately hot iron or otherwise; (4) the characters must not fade when repeatedly washed with soap and water, and must resist the action of acids, alkalies, and bleaching powder; and (5) it must be stable in the bottle and not gelatinize or form deposits if exposed to the air for any length of time. Marking inks are so varied in composition that no specific directions for analysis can be given; the analyst must decide in each case what procedure to follow.

5. ANALYSIS OF CANCELING INKS

(a) PREPARATION AND CARE OF THE SAMPLE.—Since canceling inks contain more or less insoluble and volatile matter, special attention must be given to the preparation and care of the sample. The ink must be carefully mixed by shaking before any is removed and the container should be kept open only long enough to remove the portions necessary for analysis.

(b) DETERMINATION OF MATTER VOLATILE AT ORDINARY TEMPERATURE.—This test is necessary only when the ink in the canceling machine is exposed. Place a quantity of the ink, about 5 g, in a weighed evaporating dish and let it stand exposed to the air. Reweigh after 18 hours, and then after each day. Calculate the percentage of loss after each weighing. The loss should not exceed 15 per cent during the first seven days.

(c) PENETRATION TEST.—(1) *Apparatus*.—The apparatus required includes: (a) Homeopathic shell vials about 8 cm long and 2 to 2.5 cm in diameter. (b) Strips of white blotting paper, which for a given series of determinations should be cut from the same sheet and of exactly the same dimensions. A convenient size is 12 mm wide and 25 cm long. (c) A pair of dividers with arms 15 cm long or longer. (d) A millimeter rule.

(2) *Determination*.—Place approximately 5 cc of the ink or other material to be tested in one of the "shell vials" described, and if several samples are to be tested, arrange the vials in a row. Place 5 cc portions of distilled water in each of two vials and put one vial containing water at each end of the row of vials containing samples to be tested. Proceeding from left to right, insert a strip of blotting paper in each of the vials and record the exact time. The blotting paper should maintain a nearly upright position. The liquids gradually ascend the strips by capillarity; the strips should be in such a position that the liquid does not ascend by capillarity between the edges of the strips and the sides of the vials.

At the expiration of exactly 15 minutes from the time each strip is inserted in a vial measure by means of a pair of dividers the height to which the liquid has ascended the strip of paper and record the distance in millimeters. Make a second set of readings at the end of 45 minutes.

After all the measurements have been recorded, reduce the results to terms of the penetrating power of distilled water, represented as 100. This is accomplished by dividing each result by the average of the results obtained for distilled water and multiplying the quotient by 100. Ten samples may conveniently be tested at one time by working as described. The method gives good comparative results and has been applied not only to canceling and other stamping inks but to the liquids used for the manufacture of these inks.

In observing the penetrating power of a given sample of ink it is important to remember that the value of a canceling or stamping ink depends upon its power to penetrate the paper during the first minute or fraction of a minute after its application to the paper. It is well, however, to keep the tests under observation for several hours, as information can thus be obtained in regard to the extent to which the coloring matter follows the liquid base of the ink as it passes through the paper. In some cases the coloring matters keep pace with the liquid portions of the ink; in others an uncolored band at the top of the portion of the paper which is wet with the ink shows that the coloring matter does not proceed through the paper as rapidly as the base of the ink. This may or may not be undesirable. If the colorless band is due to a difference in the rate of penetration, it is undesirable. If it shows that the dye contained in the ink has an affinity for the fibers of the paper, it is evidence of a valuable quality.

Additional information can be obtained from the penetration test by removing the strips of paper from the vials, cutting off the part of the paper which has actually been immersed in the ink, and treating the upper part successively with petroleum ether, alcohol, and other solvents for removal of the constituents of the ink. The extent to which the dye or dyes contained in the ink resist the action of these solvents and the extent to which the lampblack has passed up the strip of blotting paper are indices of the quality of the ink.

An examination of the strips through a microscope will give valuable information regarding the rise of carbon in the paper and the affinity of the dye for the fiber of the paper. With many

inks the carbon will not rise above the surface of the liquid, while with others it penetrates the paper to the same height as the dye. With this class of inks it is important that the base of the ink have the power to carry the carbon well into the fibers of the paper.

To make the determination allow the strips to remain in position until the next day, remove, dry between blotters, and examine for a rise of dye or carbon. If either dye or carbon rises as far, or nearly as far, as the base of the ink, the rise is pronounced "satisfactory." Less than this is not acceptable except in the case of glycerol inks, which rarely give any rise of carbon. A small amount of rise in the latter inks must be accepted as satisfactory. To determine whether the coloring matter is carbon or simply dye, pick off particles of the paper and adhering ink at intervals on the strip and mount on slides with water or alcohol. Examine with the microscope, using low power; note the size of the carbon grains. The grains adhere to the outside of the paper fibers in clots, as a rule, but it is often difficult to distinguish them.

(d) **SEDIMENTATION TEST.**—(1) *Apparatus.*—(a) Glass-stoppered cylinder, graduated for 200 cc and fractions thereof, the distance between the bottom and the 200 cc mark being 25 cm. If unobtainable, other cylinders may be substituted, marks being placed at distances 25 cm and 16 mm from the bottom. (b) A pair of dividers with arms 15 cm long or longer. (c) A millimeter rule. (d) Pipettes made from straight tubing (7 mm bore), at least 30 cm in length, and having a capacity of from 10 to 15 cc.

(2) *Determination.*—By means of the special pipette introduce the ink carefully, drop by drop, into one of the 200 cc cylinders, to a depth of exactly 16 mm. The ink should be previously tested to ascertain a proper solvent for both base and dye. Alcohol is generally the solvent to use for rosin inks. It may be necessary to use other solvents, such as gasoline (boiling point 50° to 60° C), ether, benzene (benzol), etc. Dissolve the ink in the cylinder in the appropriate solvent, dilute to the 200 cc mark, stopper, and shake thoroughly. Allow the cylinder to stand and record from time to time, by using the dividers and millimeter rule, the height of the top of the layer of sediment which collects in the bottom of the cylinder, expressing the results in millimeters. During the first hour observations should be made at intervals of 15 minutes; later, each hour for several hours successively, and then twice daily for a week to 10 days.

After settling has entirely ceased the height of the sediment should equal or exceed 16 mm., the original height of the ink. The rate of sedimentation is an index of the state of division of the carbon, some inks showing no appreciable layer at the expiration of a 10-day test.

In the case of some inks the supernatant liquid above the sediment is of such a dark color that there is difficulty in locating the top of the sediment, even when the cylinder is examined by light reflected at various angles. In this event the use of a dark room with a light placed so as to give a strong ray through a small aperture will locate the top of the layer of sediment in all cases except when the ink contains a very large percentage of an intense dye.

Frequently the layer may be located by holding an incandescent electric light back of the cylinder and noting where the lamp filament can not be seen. The test is somewhat crude and only approximate, but it serves to give an idea of the fineness and amount of carbon, and, as a rule, agrees fairly with the carbon determinations.

(e) DETERMINATION OF LAMPBLACK.—Weigh about 5 g of ink in a small beaker, dilute with a suitable solvent (alcohol is used in case of rosin-oil inks), let stand until the carbon settles, transfer to the Gooch crucible, and wash until all oil and soluble color are removed. Finally, wash with alcohol and ether, dry, and weigh. This weight is to be corrected for the amount of ash.

(f) DETERMINATION OF ASH.—The lampblack prepared for the manufacture of canceling ink should yield less than 0.5 per cent of ash when burned, and the coal-tar dyes employed should contain no mineral matter other than that which is an essential part of the molecules of the substances to which the tinctorial power of these dyes is due.

For the determination of the ash place 2 to 3 g of the ink in a porcelain dish, which must be of such size as to prevent loss of ink due to the foaming which is likely to attend the beginning of the incineration. Heat the dish thus charged in a muffle at a low red heat until all organic matter and uncombined carbon have been burned. Cool and weigh.

If an excessive amount of ash is found, the percentage of mineral matter contained in the alcohol extract should be determined by incineration of the residue obtained after evaporation of this extract. If either the total ash or the ash of the alcoholic extract is high, a qualitative examination should be made.

(g) RESISTANCE OF PIGMENTS AND DYES TO LIGHT AND REAGENTS.—It is necessary, in the case of canceling inks and important, if not necessary, in the case of stamping inks that the pigments and dyes employed in their manufacture be as resistant as possible to means which may be employed for the erasure of marks made with them on paper. Under this heading may be mentioned also the importance of the use of dyes which possess considerable affinity for vegetable fibers. It is not desirable to enumerate the agents which should be employed in experiments to ascertain the resistance of a given dye to erasure, since light, heat, and all of the solvents and reagents known to the chemist are available for the use of persons who might desire them for making fraudulent erasures.

For the purpose of canceling postage stamps it is necessary that the canceling marks be substantially indelible, because the inks used in printing many of the stamps are very resistant. Stamping inks used for other purposes, however, do not require absolute indelibility.

In making the tests use several layers of blotting paper as a pad, pour on this a small quantity of the ink and distribute carefully; see that all excess has been absorbed by the pad before using the stamp. Make on paper a sufficient number of impressions at one time to suffice for all tests and leave some in reserve. Having made the impressions, arrange them in groups according to the color and kind of the ink, and rank them according to the following scheme: (1) Of highest rank, (2) very good, but not of the best, (3) good, (4) fair, and (5) poor.

Having exposed the impressions to the various reagents as described hereinafter, each sample is again rated according to the effect of the reagents, as follows: (1) Unaffected, (2) slightly affected, (3) much affected, (4) almost effaced, and (5) effaced.

The wet reagents used are pure water, water with the addition of 10 per cent of strong ammonia (sp. gr. 0.90), pure alcohol (95 per cent), alcohol with the addition of 10 per cent of strong ammonia; 2 per cent hydrochloric acid, and $\frac{N}{200}$ bleaching powder solution. Expose each impression in a small Erlenmeyer flask to about 50 cc. of the reagent for 24 hours, noting its appearance at the end of 15 minutes, 1 hour, and 24 hours. Then rinse, dry, and rate.

For the light test expose the impressions to the ultra-violet light for 48 hours. The tests with reagents are considered of less use than the other tests and are not always applied.

6. ANALYSIS OF STAMPING INKS

(a) PREPARATION AND CARE OF SAMPLE.—The precautions given in regard to the care of samples of inks made with an oil base should be observed.

(b) CHANGE OF WEIGHT ON EXPOSURE TO AIR.—The determination should be conducted in the manner described for the determination of volatile matter in inks made with an oil base. Rubber-stamp inks, however, gain or lose in weight according to atmospheric conditions. A rubber-stamp ink should not, however, undergo very much greater changes in weight when exposed to the air under given conditions than diluted glycerol containing 75 per cent of glycerol and 25 per cent of water by volume.

(c) PENETRATING POWER.—This test should be conducted in the manner described for inks made with an oil base.

(d) SEDIMENTATION TEST.—This test should be conducted as described for inks made with an oil base, with the exception that the portions of ink should be diluted with water instead of with organic solvents.

(e) DETERMINATION OF LAMPBLACK AND OTHER CONSTITUENTS.—A scheme of analysis similar to that described for inks made with an oil base should be employed.

(f) RESISTANCE TO LIGHT AND REAGENTS.—The remarks made in regard to the investigation of the resistance of cancellations made with oil inks apply, in general, to canceling and other inks for use with rubber stamps.

(g) SPECIFIC GRAVITY.—Determine by means of a picnometer at 15.6° C and refer to water at the same temperature.

(h) SUGARS.—In the manufacture of some canceling inks glucose is used in place of glycerol. To determine the amount of glucose present weigh about 3 g. of ink and dilute in a beaker with a little water. No definite scheme for removing the dyes can be given. Many of the dyes used in stamping inks are precipitated with sodium hydroxide and may be filtered off, and the sugars determined in the filtrate, which must be diluted to 200 or 250 cc in a volumetric flask. Place 30 cc of Fehling solution A, 30 cc of solution B, and 60 cc of water in a beaker and heat to boiling.

Add 25 cc of the solution of the material to be tested, which must be so prepared as to contain not more than 0.250 g of dextrose, and boil for two minutes. Filter immediately in a weighed Gooch crucible and obtain the weight of copper oxide. The corresponding weight of dextrose may be found from Allihns' Table, Bulletin No. 107, Bureau of Chemistry, page 51.²

7. ANALYSIS OF DUPLICATING INKS

(a) CARBON.—Determine as in "5. Analysis of Canceling Inks."

(b) ASH.—The ash material will usually give an indication of the pigment used other than carbon.

(c) OILS.—There is no definite method of identifying mixtures of oils. However, a few simple tests will give some indication of the nature of the oils present. The presence of rosin oil may be detected by the Liebermann-Storch reaction; sulphonated castor oils and rosin soaps are soluble in water; castor oil is easily detected by its odor and also by its solubility in alcohol.

The iodine number gives some indication of the nature of the oils present. It can by no means be taken as a reliable indication of the composition. Duplicating ink is given a practical test. If it works well in a duplicating machine and reproduces clearly, it is considered suitable for the purpose.

8. EXAMINATION OF DOCUMENTS FOR INVISIBLE WRITING

Apart from the application of heat and light, it is obvious that many chemical reagents must be applied to discover the presence of invisible writing. These are applied on the end of a feather to various parts of the document.

It is for obvious reasons inadvisable to describe any routine method of examination. It is quite an easy matter to ascertain whether in the case of invisible writing done with a cobalt salt the chloride or the nitrate was used. If a drop of silver nitrate is placed on one of the letters and examined under the microscope, an opalescence will gradually spread through the drop if chloride is present. Again, if a minute drop of sulphuric acid and a few particles of brucine are applied to another letter, a blood-red coloration will result if a nitrate is present.

² See also Walker and Munson, *J. Amer. Chem. Soc.*, 28, p. 512: 1906.

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