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INKS
TYPEWRITER RIBBONS
AND
CARBON PAPER

CIRCULAR OF THE BUREAU OF STANDARDS, No. 95

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INKS, TYPEWRITER RIBBONS, AND CARBON PAPER[1]

ABSTRACT

This circular contains a discussion of the composition and methods of testing inks, typewriter ribbons, and carbon paper. The methods are not original, but have been compiled from a variety of sources, and modifications have been introduced when necessary.

CONTENTS

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[1] Revised by I. M. Welch.

I. INTRODUCTION

The origin of ink belongs to an era following the invention of writing, when the development of that art had advanced beyond the stage of stone inscriptions or clay tablets. Some material for marking with reed or brush was necessary. It was not difficult to obtain black or colored mixtures for this purpose. With their advent 40 or more centuries ago we find the origin of ink.

About 1,200 years before the Christian era the Chinese invented "India ink," which "was obtained from soot, produced from the smoke of pines and the oil in lamps, mixed with the isinglass of asses' skins and musk to correct the odor of the oil." The Hebrews and the Arabians had similar methods for making ink. The ancients also knew the use of a brown color, sepia, which is the secretion of a small gland of the cuttle fish.

The Greeks and Romans seemed to prefer the stylus with its accompanying sheets or tablets of ivory, wood, metal, or wax, although the use of ink was known to them. It was not until about 200 A. D. that the employment of ink again became popular. Silver inks, red inks made of vermilion or cinnabar, blue inks of indigo, and inks of Tyrian purple were used, as well as the India ink manufactured by the Chinese, which was imported in preference to that of similar character made at home.

In the first half of the twelfth century the iron-gall or modern ink of to-day came into vogue. About 1126 A. D. a formula appeared for an ink which was a mixture of an infusion of nutgalls, green vitriol (ferrous sulphate), and fish glue. At about the same time the introduction of flax or linen paper provided a suitable material on which to write with ink of this type.

William Lewis, in 1748, has the credit of being the first to make writing fluids the subject of scientific experiments and to draw conclusions as to the proportions of the various ingredients required to make a really permanent ink.

The earlier inks made from nutgalls and ferrous sulphate were muddy liquids because they were allowed to age until they became black, owing to the formation of ferric gallotannate by the action of atmospheric oxygen upon the pale blue or green ferrous gallotannate. The latter is soluble in water, but the black ferric compound is insoluble and separates in fine particles. The settling of these black particles was more or less completely prevented by the addition of glue or gum to the ink. This also served to hold the particles to the surface of the paper, because they could not penetrate between the fibers and would be rubbed off easily unless there were something to make them adhere.

A great step in advance was taken in the early part of the nineteenth century, when inks of the kind now in general use were first made. These inks are not allowed to become oxidized, and, therefore, black and muddy before use, but are clear fluids, which penetrate into the paper. The black ferric gallotannate is formed between and upon the fibers of the paper, and writing so made is more difficult to erase by scraping or by the action of chemicals than is writing with the older kind of ink.

There are certain disadvantages connected with the modern inks. In order to retard the oxidizing action of the air as much as possible, an acid must be added to the ink. This delays the precipitation of the black, insoluble iron gallotannate, but causes corrosion of steel pens. Sulphuric and hydrochloric acids are most commonly used, and both readily dissolve steel. When the ink dries on paper, the hydrochloric acid evaporates, but any excess of sulphuric acid remains and may disintegrate the fibers. Acid sulphates and organic acids, such as salicylic, are occasionally substituted for the two mineral acids mentioned. They are especially useful in ink powders and tablets.

Another disadvantage of the modern inks is that the iron compound which is in the clear solution would give such pale writing at first that it is necessary to add a dye to make the characters easily legible. The dye does not increase the permanence of the writing, and is masked in a few days by the black color of the iron compound that is formed. Blue has always been the preferred color to add to writing inks, and "blue-black" is usually seen on the labels of ink bottles. Indigo was first used because it is practically the only natural blue dye. Plant dyes of other colors were occasionally employed, but were not so popular as indigo. Synthetic dyes have now almost, if not entirely, supplanted indigo in iron gallotannate inks. Any water-soluble blue dye which is not precipitated by the acids or by the tannin in the ink may be used. The same is true of other dyes which are used to make red-black, purple-black, and black-black inks.

In 1890 Schluttig and Neumann, after extensive investigations, published a formula which they believed would give the best possible iron gallotannate ink. The formula called for an amount of ferrous sulphate equivalent to 6 g of metallic iron, and appropriate amounts of other ingredients, in a liter (about 1 quart) of ink. This ink was adopted by the State of Massachusetts as the standard for all official purposes. In 1912 the Prussian Government issued regulations requiring that documentary or record inks should contain at least 4 and not more than 6 g of iron in 1 liter.

The United States Government incorporated in its specification for "Treasury Standard" writing fluid the requirement that ink furnished shall be equal in every essential to a standard ink made according to the formula adopted by the State of Massachusetts.

The tannins are a group of more or less closely related chemical compounds that are found in plants. They are so called because of their being used to make leather by the tanning of hides. Some of the commercial sources of tannin are chestnut, oak, and hemlock barks, sumac, divi-divi, myrobalans, valonia, and mangrove.

The tannic acid mentioned further on in the formula for a standard ink, is the tannin from nutgalls. These are excrescences found on the twigs, leaves, and other parts of plants, especially of the oak. Various kinds of insects lay their eggs in the plant tissues and this, for some reason not fully understood, causes an abnormal growth at the center of which the eggs hatch and the grubs develop and mature. The shape and size of the gall are characteristic of the kind of insect that produces it. Galls vary in size from the minute "flea seed" found in California to the ones several inches in diameter which are found on the roots of certain oaks. The ordinary nutgalls of commerce are known commonly as Aleppo, Turkey, or Levant, and Chinese galls. The blue or green galls from which the insects have not escaped are more valuable because they have a higher content of tannin than the white galls.

Tannins vary greatly; they are described as iron-bluing or iron-greening according to the color they produce with ferric salts. The difference is apparently one of chemical constitution. All of the tannins contain what the chemist knows as "hydroxyl groups," and they can, therefore, be classed as phenol derivatives. The simplest possible member of the class is ordinary phenol, or carbolic acid, which has one hydroxyl group. The tannins differ from one another in the number and arrangement of the hydroxyl and other atomic groups they contain.

Schluttig and Neumann made a series of tests with 28 phenol derivatives in combination with ferric salts. Some gave no color; others, such as phenol and resorcinol, gave a very pale violet; still others, such as salicylic acid, gave a darker color which faded rapidly on exposure to light and water. Other colors varying from brown or yellow to black were produced by others of the substances studied. The general conclusion was that the only substances which could be relied upon to give a permanent deep color with iron salts were those which contained three free adjacent hydroxyl groups. This arrangement of the atoms is found in the tannic acid from nutgalls and in the closely related gallic acid.

The ferrous sulphate, also called green vitriol and copperas, which is used in making ink, is one of the commonest and cheapest chemicals. It can be made by dissolving iron in dilute sulphuric acid, but it is produced in such large quantities as a by-product in some industries that there is always an abundance of it from these sources. As already explained, atmospheric oxygen changes the nearly colorless, easily soluble ferrous gallotannate to black, insoluble ferric gallotannate. This causes the blackening of writing made with modern inks, and was what made the old-time inks muddy, because they contained no free acid to hold the iron compound in solution. The formation of black sediment in bottles of modern ink is due to somewhat different chemical changes. Hinrichsen analyzed clear ink that had been freed from sediment by filtering, and found that it contained as much iron as the ink before the deposit formed. In other words, the deposit contained practically no iron. He also found that the liquid filtered from the sediment contained less gallic and tannic acid than the fresh ink. The sediment was, therefore, not iron gallotannate, but was composed of products formed from the tannins.

Although ferrous sulphate has been used with success as an antiseptic for some purposes, the amount of it in ink is not sufficient to prevent the growth of bacteria and molds. A preservative, such as phenol (carbolic acid) must, therefore, be used in the ink. Phenol has an odor that is objectionable to many persons, and it is quite poisonous. For that reason the use of the odorless and less poisonous salicylic and benzoic acids has been suggested.

Before the discovery of the first synthetic dye in 1856, inks of other colors than black were perforce made from natural coloring materials. Thus red ink was a solution of carmine, a dye obtained from the cochineal insect. Some manufacturers to-day sell what they call carmine inks, although they are made from synthetic dyes.

The synthetic dyes, also called "coal-tar colors" and less correctly "aniline dyes," are made in such a variety of shades and have such intense colors that it was natural to think of using them for making ink. The first to be used for this purpose was Hofmann's violet, discovered in 1863. Other colors were used later. Even to-day some inks on the market are solutions of dyes, although their fugitive nature is well recognized. The subject was investigated by the Prussian Government in 1879, and the use of inks made from synthetic dyes was prohibited for documentary writing because of their lack of permanence.

II. TYPES OF WRITING INKS

No matter of what material it is made, writing ink must be 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 heat, and to the action of chemicals. The durability is judged by the freedom from formation of scum, sediment, and mold. The writing quality is a factor which must also be taken into consideration inasmuch as some inks, in spite of excellent durability and permanence, are unsuited for pen work because of improper consistency, high acidity which causes excessive corrosion of pens, or insufficient color.

The specific use for which an ink is intended must be considered in estimating its quality. If permanence is most essential, durability and writing quality must be somewhat sacrificed; on the other hand, if great fluidity and freedom from formation of scum and sediment are of prime importance, as in fountain-pen use, it must be at the expense of permanence.

1. GALLOTANNATE OF IRON INKS

The composition and characteristics of iron gallotannate inks have already been discussed. It has been seen that ink of sufficient permanence for use on important records must contain from 4 to 6 g of metallic iron, in the form of ferrous sulphate, in 1 liter. It must also contain enough of suitable tannins to combine with the iron and produce black writing. Ink of this concentration, on account of its rather heavy body, its corrosive action on steel pens, and other objectionable features, is not popular with those who are compelled to use it. The United States Government has recognized these faults by adopting two specifications, one for record ink and one for a more dilute ink that may be used for ordinary purposes.

Further discussion of the composition and characteristics of iron gallotannate inks will be found in the following paragraphs.

(*a*) WRITING INK.—Writing ink is suitable for use in fountain pens or with ordinary steel pens. Writing made with it is as permanent as most paper now used. One press copy can be made while the writing is fresh. The writing ink purchased by the United States Government must be as good in every essential as ink made according to the formula given below. It is not required that the inks furnished by the manufacturer shall be made of the pure materials specified in the formula. The best grades of writing and fountain pen inks now available on the market are similar to this ink.

	Grams
Tannic acid	11.7
Gallic acid	3.8
Ferrous sulphate	15.0
Hydrochloric acid, dilute, U. S. P	12.5
Carbolic acid (phenol)	1.0
Soluble blue, Schultz No. 539 (Col. Ind. No. 707)	[2] 3.5

Water to make a volume of 1,000 cc at 20° C.

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[2] There are many different kinds of dyes, most of which have more than one name, because each manufacturer likes to have distinctive names for his own products. In order to avoid uncertainty and confusion when speaking or writing about a given dye it is becoming customary not only to call it by name but also to give its serial number in one of the following books. These books classify and tabulate the dyes. The German book is the older and better known. Gustav Schultz, Farbstofftabellen, 5th ed.; 1914. Society of Dyers and Colourists, Colour Index, 1st ed.; 1924.

Concentrated ink is in the form of a thick liquid and is usually sold in small bottles containing a sufficient amount of the ingredients to give 1 quart of ink of the desired strength. The paste which is sold in collapsible tubes contains still less water than the concentrated ink.

The powders and tablets are mixtures of the dry ingredients. Most of the powders and tablets are composed entirely of dyes, and, therefore, do not make permanent ink. A few kinds contain the ingredients of iron gallotannate ink. In these, solid organic acids or acid salts of mineral acids are used instead of hydrochloric or sulphuric acid. Failure to use material of an acid nature will result in a powder which, when dissolved in water, will have a tendency to form a thick scum or sediment in a few days. It is not possible to use the dried and ground residue from ordinary ink. If hydrochloric acid is used, it will escape as the water evaporates; sulphuric acid as it becomes concentrated will char and destroy part of the tannin and dye; any remaining tannin will form an insoluble compound with the iron.

Concentrated ink, powders, and tablets possess certain definite advantages. A quart bottle of writing fluid ready for shipment weighs about 5 pounds and occupies about 275 cubic inches, whereas the quantity of concentrated liquid sufficient to make a quart of the fluid occupies about one-fourth that space. A corresponding amount of powder or tablets weighs approximately 2 ounces and occupies 8 cubic inches. The particular advantage of the dry ink is the great reduction in breakage, which entails not only loss of the ink but also the probability of ruining other articles. The danger of freezing is entirely eliminated. Another point worthy of consideration is the superior keeping quality of the dry powder over a liquid. The concentrated liquid, on the other hand, possesses the advantage of being more readily soluble than the powders, and has less tendency to form a sediment or scum, because it can contain the requisite amount of mineral acid to keep the iron in solution. Concentrated ink freezes at a lower temperature than the more dilute writing fluid.

There are a few objections to the use of ink which must be prepared in liquid form by the consumer; the user must furnish his own container; careless persons may not make up the ink properly; and the water in certain localities may contain ingredients deleterious to the ink.

(*b*) Record and Copying Ink.—For records where permanence is the chief factor, as in signing important documents, an ink of the strength prescribed in the following formula is necessary. This ink is based on the formula developed by Schluttig and Neumann and later adopted by the State of Massachusetts and the United States Government.

	Grams
Tannic acid	23.4
Gallic acid	7.7
Ferrous sulphate	30.0
Hydrochloric acid, dilute, U. S. P	25.0
Carbolic acid (phenol)	1.0
Soluble blue, Schultz No. 539 (Col. Ind. No. 707)	3.5
Water to make a volume of 1,000 cc at 20° C.	

Record and copying inks can also be obtained in the concentrated and solid forms, but the ingredients are more difficult to dissolve in this concentration.

(*c*) COPYING INK.—The record and copying ink just described is suitable for making one press copy when the writing is fresh. If several copies are desired, a special copying ink must be used. An additional amount of coloring matter is essential, together with a certain amount of gum or other adhesive to bind the excess of coloring matter to the paper and to prevent too rapid oxidation. Dextrin is sometimes added in place of gum. Sugar, too, is frequently used; 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 is to prevent the gum from completely drying. If, however, it is added in excess the ink will smudge. Because these additional ingredients are all soluble in water they facilitate the making of press copies. Below is the formula of a typical copying ink:

	Grams
Tannic acid	46.8
Gallic acid	15.4
Ferrous sulphate	60.0
Hydrochloric acid, dilute, U. S. P	50.0
Gum arabic	10.0
Carbolic acid (phenol)	1.0
Soluble blue, Schultz No. 539 (Col. Ind. No. 707)	5.0
Water to make a volume of 1,000 cc at 20° C.	

(*d*) AGE OF QUESTIONED DOCUMENTS.—In many litigations the decision of the court hinges upon the authenticity of documents that have a bearing upon the case. The point at issue may be the genuineness of a signature or of a date, and often a knowledge of the approximate age of the writing will help to decide this.

There are books and magazine articles on the subject, and experts who make their living by testifying in courts all over the country. The underlying principles are simple enough in theory, but are greatly complicated in practice. Only an outline of the procedure followed in attempting to decide the age of writing can be given here.

Because the documents are usually wills, deeds, and similar official records, and in any case must not be destroyed or damaged, it is evident that chemical reagents can be applied only to small portions of the writing. The procedure followed in an actual examination may be of interest as showing how the tests are made and what precautions are taken. The object was to find out whether one of the signatures on a document was a few months or several years old.

The examination was made in the presence of a court officer and of lawyers and experts representing both sides. By mutual consent one of the chemists applied a small drop of a reagent with a thin glass-stirring rod to part of one of the letters, at the same time dictating a statement about the reagent he was applying and to what part of a particular letter of a word. The document was then passed around without comment so that each person could draw his own conclusions from what he observed. Proceeding in this way all of the writing was successively tested with water and chemical reagents, and press copies were made. With these somewhat elaborate precautions every possible kind and age of ink on the paper was examined in a way that did not invalidate the document as evidence, there was an official record of what reagents were applied and where, and one examination sufficed for the experts on both sides.

That a knowledge of the history of the ink industry may be helpful in establishing the age of writing is shown by the examination of a certain writing in red ink.[3] It was proved that the writing could not have been made at the time alleged, 1868, because tests showed that the coloring matter was eosine. This dye was not discovered until 1874, and was not used for making ink until several years later.

Generally the difficulties are much greater than in this ideally simple case. Writing with a blue-black iron gallotannate ink undergoes the following series of changes: It is at first more or less intensely blue, according to the kind and amount of dye in the ink. As the air acts upon it the writing becomes blacker until it reaches its greatest intensity, which depends upon the amounts of iron and tannin. It is then black with more or less of a bluish tone. With increasing age the blue dye is gradually destroyed by the action of the air and only the iron compound is left. This, too, is not permanent, but is slowly oxidized and becomes increasingly browner until eventually only a rusty stain of iron oxide is left on the paper.

When the writing is new the dye will "bleed" out when water is applied to it, and strong press copies can be made. As the dye is gradually oxidized away the bleeding and the press copies become

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[3] Carvalho, Forty Centuries of Ink, p. 227.

weaker and weaker, until no more dye can be detected. How long the blue dye lasts depends upon its kind and amount, and upon how the writing is kept. In the dark, 10 or 20 years may not suffice to destroy the dye, but all will be gone in a much shorter time if the writing is much exposed to bright light, which hastens its oxidation.

Chemicals that may readily bleach, dissolve, or otherwise change fresh writing do not act so readily when it is older, but here again much depends upon the ink and how the writing has been kept.

The preceding four paragraphs give an idea of the kind of study that must be made of writing to determine its approximate age. Some of the factors that make the task difficult are the following: Uncertainty about the composition of the ink—that is, the amounts of iron, tannin, and dye it contained; the kind of dye; whether a stub or fine pen point was used; whether the writing was blotted or allowed to dry; whether the ink soaked into the paper or remained chiefly on the surface fibers; how the writing has been kept.

2. CARBON INKS

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

India or Chinese ink is made from carbon and suitable binding materials. When carbonaceous products, such as natural gas, oil, resins, or tar, are burned with an insufficient supply of air, carbon is formed. The material is 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. The ink appears on the market in solid sticks, which are rubbed up with water when ready for use.

Modern carbon inks are made from mixtures of gum arabic, shellac, and borax, with carbon in suspension. The borax reacts with the shellac to form a soap which is soluble in water, but which after drying forms an insoluble film on paper. The gum arabic acts as a so-called protective colloid. It is generally assumed that the small particles of carbon attract coverings of the gum to themselves. Inasmuch as colloids can not diffuse through colloids, these small particles can not get together and form particles large enough to settle out, and so remain in suspension. This is the most probable hypothesis yet advanced to account for the facts, but this mechanism of a protective coating has not yet been convincingly demonstrated by experimental work. Inks of this type find their widest application as waterproof drawing inks, although there are a few brands manufactured for ordinary writing purposes.

3. DYESTUFF INKS

In the manufacture of inks which need not possess permanence aqueous solutions of synthetic dyes can be used. For ordinary writing purposes these inks are very satisfactory because they contain no acid which will corrode steel pens. Water-soluble synthetic dyes provide a variety of colors: Crocein scarlet, Schultz No. 227 (Col. Ind. No. 252); malachite green, Schultz No. 495 (Col. Ind. No. 657); soluble blue, Schultz No. 539 (Col. Ind. No. 707); methyl violet, Schultz No. 515 (Col. Ind. No. 680); and nigrosine, Schultz No. 700 (Col. Ind. No. 865), which last possesses considerable permanence. The following formula produces a satisfactory red ink. Other colors can be obtained by substituting one of the dyes in the foregoing list.

Dissolve 5.5 g of crocein scarlet, Schultz No. 227 (Col. Ind. No. 252), in 1,000 cc of distilled or rain water at 20° C.

A material formerly commonly used for inks is logwood. The logwood chips are digested with hot water and the extract obtained is used for coloring. The coloring matter, hematoxylin, becomes purple on oxidation. Since it contains three adjacent hydroxyl groups it follows the general rule established by Schluttig and Neumann of yielding an ink with iron salts. Chrome logwood ink, made by adding a small amount of potassium chromate to a decoction of logwood, is, however, the most common. Copper logwood inks are made by boiling alum, copper sulphate, and logwood, and filtering the solution. The filtrate, which is red-violet, writes a pure violet and then rapidly darkens.

Prussian blue in its soluble form is used for inks. Pure Prussian blue is ferric ferrocyanide. The commercial product is a mixture of true Prussian blue with Turnbull's blue, Williamson's blue, and other cyanides of iron. It is prepared by adding solutions of ferric salts to solutions of ferrocyanides. If an excess of ferrocyanide is present, a precipitate containing alkali is obtained which is soluble in water. Soluble Prussian blue can also be prepared by mixing pasty Prussian blue with oxalic acid solution, allowing the mixture to stand for some time and then separating the oxalic acid with alcohol. Treatment of Prussian blue with alkali hydroxides results in the quantitative formation of alkali ferrocyanide and ferric hydroxide.

Prussian blue inks have an intense blue color which does not darken on exposure to the light and air. They show no appreciable fading in the light and are not affected by most acids and commercial ink eradicators. However, the pigment is soluble in oxalic acid and it is readily decomposed by alkali according to the reaction described above. Even as weak an alkali as soap and water will completely remove from paper writing made with Prussian blue ink.

4. HECTOGRAPH INKS

A method for producing duplicate copies, which finds a limited use where carbon copies are not feasible, is by means of the hectograph. The hectograph is either a clay or a glue-glycerol mixture which presents a sufficiently moist surface to absorb some of the dye from the writing which is placed in contact with it. A reversed impression is produced on the hectograph. From this, copies are made on fresh sheets of paper by placing them in contact with its surface for a few seconds. The number of copies obtainable depends largely on the nature of the ink with which the writing was made.

The ink contains a large amount of water-soluble dye and a hygroscopic substance, such as glycerol or glucose, to make the writing more readily transferable to the hectograph surface. Crystal violet, Schultz No. 516 (Col. Ind. No. 681), is probably the most satisfactory dye.

As most of the dyes used are fugitive when exposed to light, hectograph copies can not be relied upon for permanent records.

5. INDELIBLE INKS

Of the different substances that have been employed as indelible inks the best known and most commonly used in the past has been a solution of a silver salt. This, on reduction in the fiber, leaves an insoluble black deposit of finely divided silver, which is more or less permanent. Heat or exposure to sunlight is required for the development of the color. A temporary color is provided by a pigment or dye. A typical silver marking ink was found to contain water, silver, tartaric acid, ammonia, gum, and a pigment. Salts of other metals, such as gold and molybdenum, and the sulphides of iron, or copper, or organic substances, such as nonvolatile fats, in the presence of a suitable metallic hydroxide or sulphide have been used.

A type of ink more recently developed consists of a solution of dye, such as unsulphonated nigrosine, in aniline, phenol, or cresol. These inks require no special methods of application and are suitable for use in automatic marking machines.

The quality of an indelible marking ink is judged by its color when properly developed, the penetration of the fiber to which it is applied, the absence of injurious effects upon the fiber, and its permanence in light and to washing.

Indelible inks are of two types. Those intended for general household and laundry use must dry rapidly and penetrate the starch and other sizing materials. In many cases the articles are laundered immediately after marking. These inks are, in general, more permanent, but may destroy the fabric unless the excess of ink is removed soon after application. For marking blankets, sheets, and other unsized articles which are to be stored on shelves for indefinite periods, ink of a different kind is necessary. It may be slow drying but it must contain no ingredients which will be harmful to the fiber. It must not contain a solvent which, as it evaporates, will produce a stained zone around the actual marks.

6. 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.

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 it 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.

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.

Lemery (1720) described sympathetic inks which appear to have consisted of lead acetate, the writing being made visible by applying a solution of a sulphide or by exposing it to the fumes of ammonium sulphide.

Writing made with a dilute solution of sulphuric acid turns black on the application of heat. A solution of ammonium chloride, developed with heat, is also effective and there is less danger of destroying the paper. Lemon and onion juices are turned brown by heat.

III. TYPES OF OTHER INKS

1. STAMP-PAD INKS

Ink used for rubber stamps should contain such ingredients that it will give sharp and intensely colored impressions which dry rapidly. The ink should not dry, or become too moist or cake on the pad. Most stamping inks are made from glycerol and synthetic dyes. The quick-drying variety, however, has as a base an organic solvent, such as acetone, methyl alcohol, or ethyl acetate. The manufacture is quite simple, because the inks are solutions of dyes in suitable solvents. A satisfactory ink for stamp pads can be made by dissolving 5 g of dye in 100 cc of 55 per cent glycerol (sp. gr. 1.1415 at 20/20° C.). Other organic solvents can be substituted for the quick-drying variety. Suitable dyes are nigrosine, Schultz No. 700 (Col. Ind. No. 865); soluble blue, Schultz No. 539 (Col. Ind.

No. 707); light green, Schultz No. 505 (Col. Ind. No. 670); magenta, Schultz No. 512 (Col. Ind. No. 677), and acid violet, Schultz No. 530 (Col. Ind. No. 698).

The dye is put into a container and the hot solvent poured over it. The mixture is then heated to about 100° C. until all of the dye is dissolved.

2. RECORDING INKS

Inks used for self-recording instruments must possess great fluidity, must dry quickly without blurring, and must contain no coarse particles which will clog the pen. They must often withstand extremes of temperature. They are similar in composition to stamp-pad inks. They are made by dissolving a suitable dye in a mixture of glycerol and water, and filtering. The ratio of glycerol to water is varied with the temperature at which the ink is to be used. For ordinary temperatures 5 per cent of glycerol is sufficient; for extremely low temperatures, such as are required by the Weather Bureau or in airplane recording devices, a 55 per cent solution is advisable. Much of the graph paper which is used in recording devices is rosin-sized and causes blurring of inks made with some kinds of dyes. It may be necessary to experiment with a few dyes of different composition before finding one suitable. Those used for stamp-pad inks are not always satisfactory in inks for recording devices. The following dyes have been used with satisfaction in inks for a multiple recording instrument: Crocein scarlet 3B, Schultz No. 227 (Col. Ind. No. 252); soluble blue, Schultz No. 539 (Col. Ind. No. 707); brilliant green B crystals, Schultz No. 499 (Col. Ind. No. 662); methyl violet 5B, Schultz No. 517 (Col. Ind. No. 683); paper yellow 3G, Schultz No. 303 (Col. Ind. No. 361); Bismarck brown Y, Schultz No. 283 (Col. Ind. No. 331); nigrosine, Schultz No. 700 (Col. Ind. No. 865).

3. CANCELING INKS

The demand for canceling inks has come almost entirely from Government departments or from manufacturers who pay the tax on articles which they produce and consequently must cancel the revenue stamps affixed to the goods. The inks are of two types—those used with rubber stamps, which have as a base, glycerol; and those used with metal stamps, which have as a base a nondrying oil mixed with a volatile thinner. The ink contains pigment and dyes, usually lampblack with a blue synthetic dye as toner. It must dry quickly so that the mail can be handled immediately after stamping, and must penetrate the fiber of the paper to such an extent that the marks can not be removed by erasure or washing without defacing the stamps sufficiently to prevent their use a second time.

4. PRINTING INKS

A brief mention of printing inks seems desirable, although they do not properly come within the scope of this circular. They are discussed in two earlier publications of this bureau.[4]

Printing inks are oil-base inks which contain pigments of the colors desired. The oil base may contain one or more of the following ingredients: Boiled linseed oil, rosin oil, mineral oil, rosin, hard or varnish gums, and soap. The proportions of these ingredients and of the pigments are varied according to the consistency the ink must have for a given kind of printing and according to the price at which it is to be sold.

IV. TYPEWRITER AND OTHER RIBBONS

In the past 25 years the use of pen and ink for business correspondence and for manuscripts and records has been superseded to a great extent by the use of the typewriter. In a discussion of ink it is, therefore, necessary to consider typewriter ribbons and carbon paper.

In the manufacture of typewriter ribbons the two materials to be considered are the fabric and the ink.

The fabric should be good quality cotton cloth, free from waste and imperfections of manufacture. The thread count, or fineness of weave, is of importance, because if the threads are too coarse and the fabric too loosely woven, the writing will not be sharp and clean-cut. The thread count per square inch should not only be sufficiently high, but also the difference between the warp and filling counts should be small. An equal number of threads in the warp and filling produces the maximum number of points of contact of the ribbon with the paper as the blow of the typewriter key forces the ribbon against the paper. The closer these points of contact are the clearer the writing. The thickness of the ribbon also affects the sharpness of the writing. A good ribbon should have a thread count of not less than 140 threads per inch of both warp and filling and the difference between the counts should not exceed 10 threads.

Before the present devices for cutting and gumming the edges of the fabric were perfected, woven edges were preferable. Now cut-edge ribbons are used almost entirely, except for a few special types of machines. Waviness of the edges is evidence of bad workmanship and increases the tendency to fraying, especially if the edges have not been properly gummed.

Two kinds of ink are used for typewriter ribbons—record and copying. The base of the ink used for record ribbons is usually a

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[4] B. S. Tech. Paper No. 39, Analysis of Printing Inks (now out of print). B. S. Circ. No. 53, Composition, Properties, and Testing of Printing Inks.

slow-drying oil like castor oil or rapeseed mixed with oleic acid. Carbon black is the most important pigment. Prussian blue is used as a toner to mask the slightly brown color of carbon black and to give the color to blue record ribbons. Pigments of other colors are ordinarily the insoluble lakes of synthetic dyes. The coloring matter is ground in a mill with the oleic acid and the mixture incorporated in the oil. The uncoated ribbon is passed through rollers, set at a definite distance apart, between which the ink is fed. The distance between the rollers controls the amount of ink applied to the ribbon.

Copying ribbons are coated with an ink containing a water-soluble dye. Glycerol alone or mixed with a sulphonated oil forms a suitable base. For black copying blue ribbons, carbon gives the original black writing. In the copy press the water-soluble blue dye present is transferred to the moistened paper.

Ribbons are supplied to the trade in three degrees of inking—light, medium, and heavy. The terms have little meaning, for each manufacturer establishes his own standard. It is the quality of the ink and not the amount applied to the fabric which determines the durability of the ribbon. The coating of a poorly but heavily inked ribbon may be exhausted before a lightly but well-inked ribbon will have ceased to give legible writing. The heavily inked ribbon tends to give writing which is not sharp and clean-cut and which will blur and rub in handling.

Ribbons containing carbon as the pigment produce writing as permanent as the paper. Writing made with ribbons of other colors should be reasonably permanent, but the dyes that are used in them can not last as long as lampblack.

Besides the permanence of the writing there are many other things to be considered in judging the quality of the ribbon. The ink must be applied to the fabric in sufficient quantity to give writing of good intensity of color, but not enough to cause blurring or to clog the type. The ink must not be so thin as to smear the paper nor so thick that it will not flow through the fabric. By writing several times with the same portion of the ribbon, the ink is partially depleted. If the ink is right, it will flow to this portion of the ribbon if allowed to rest for a short time. A satisfactory ribbon should show good "recovery" within one hour. It will have a longer useful life, other things being equal, than a ribbon that is made with too thick an ink.

A special kind of typewriter ribbon which finds a limited use is the hectograph ribbon. It is made by coating fabric of good quality with an ink containing a large amount of dye, usually crystal violet. The ribbon can be handled more easily and has less tendency to fill the type if it is coated on only one side. The ink must be suitable for making several copies when writing typed with it is transferred to a hectograph pad. This may be either a glue-glycerol mixture or a clay composition.

Ribbons for computing and recording machines are of the same general nature as typewriter ribbons. They require a fabric of high breaking strength, as there is considerable strain in operation, especially in the automatic machines. They are usually rather heavily inked. Permanence is not so important a factor as in typewriter ribbons.

V. CARBON PAPER

Carbon paper is the term applied to tissue paper coated with a waxy material in which sufficient pigment has been incorporated to give an intense color.

The tissue varies in weight from the very thin, weighing 4 pounds to a ream containing 500 sheets (20 by 30 inches), to heavy paper which may weigh 16 pounds or more to the ream, depending upon the use to which the paper is to be applied. In the trade carbon paper is known by the weight of the tissue on which it is coated. The 4-pound paper is used for making a large number of manifold copies; 5 and 7 pound papers are suitable for ordinary correspondence and reports; and the heavier papers are intended for pen and pencil work. The better grades of paper are made from 100 per cent rag stock. It gives the desired combination of firmness, toughness, and durability, with pliability. Bleached chemical pulp, coniferous pulp, manila and jute, and ground wood are used in the inferior grades of paper.

The coating has as a base fats and waxes, such as carnauba, ceresin, beeswax, and paraffin. The pigment is usually carbon with Prussian blue or a similar iron blue as a toner. Not all carbon papers are black as the name would signify. The iron blues and the synthetic dyes or their lakes are sometimes used for coloring matter. Only the writing produced with carbon can be considered as permanent. The coating is applied by passing through heated rollers. The paper is then passed between chilled rollers and cut to the desired size. Hard, soft, or medium finished papers are produced by varying the proportions of the ingredients used. The terms are only relative, since each manufacturer establishes his own standard. Soft-finished paper is best for making a large number of manifold copies, but it tends to rub and smut and is not as clean for the operator to handle as the hard-finished paper.

A good carbon paper should be clean and nonsmutting. The coating should be applied evenly and smoothly and there should be no pin holes or other imperfections. The paper should lie flat on a smooth surface for ease in handling by the operator.

VI. METHODS OF ANALYSIS AND TESTING

The purpose of the analysis of inks is to ascertain their approximate composition. In the case of inks having an oil base it is not necessary that the analysis should be of the highest accuracy, and frequently it is impossible to analyze the various mixtures of oils and dyes. Practical tests are in these cases the most reliable inasmuch as they give a direct indication of the suitability of the ink for the purpose for which it is designed. With writing inks, one of the most important tests is their resistance to light and reagents. Since 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, there is necessity for practical as well as chemical tests. Typewriter ribbons and carbon papers are judged chiefly by their performance under conditions duplicating actual use.

1. ANALYSIS AND TESTING OF GALLOTANNATE OF IRON INKS

The following procedure is suggested for testing gallotannate of iron inks:

If the ink in liquid form is received in a number of small containers, the contents should be combined in one bottle and allowed to stand for 24 hours to allow any sediment to settle. Concentrated ink or ink paste should be diluted to the proper strength, and powders and tablets dissolved in the required amount of water and allowed to settle. After 24 hours enough of the clear ink for all of the tests is drawn off in a pipette. The bottle is then slowly inverted and the amount and character of any sediment are noted. A whitish, heavy deposit usually indicates solids which have not gone into solution. A dark, gummy mass or sediment on the walls of the container indicates a separation of some of the ingredients of the ink because of improper manufacture or the age of the sample.

The ink is tested in comparison with a standard ink made according to the formulas on pages 6 and 8 for writing and record inks, respectively.

Streaks are made by allowing measured portions of about 0.6 cc each of the clear ink to flow freely across a sheet of white bond paper which is pinned to a board or clamped to a pane of glass and held at an inclination of 45°. A convenient method is as follows: A sheet of paper (11 by 5¾ inches) is held by means of clamps over a glass plate 8 inches wide supported on a frame at an angle of 45°. The pipettes are made from glass tubing having a 3.5 mm bore and a 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. For better comparison streaks of the standard are made on the same sheet as those of the sample to be tested.

When the streaks are dry, the sheet is examined on the front and reverse sides. The ink should penetrate into the fibers of the paper, but not pass through it. The streaks of the sample should have the same general form as those of the standard. A streak of a normal ink has an oval head and the rest is nearly uniform in width; a very fluid ink gives a wide head and the streak rapidly narrows down; a very concentrated ink shows little difference throughout the length of the streak.

The paper is cut into inch-wide strips at right angles to the streaks. Some of the strips are kept away from light and fumes, and others are used for making the following tests after they have been exposed to diffused daylight for one week:

After a week's exposure to diffused daylight, the streaks of the sample should be as intensely black as those of the standard.

After exposure to direct sunlight for 96 hours or at a distance of about 10 inches from an arc or ultra-violet light for 48 hours, the streaks of the sample should show no greater loss of color than those of the standard.

Strips are soaked in bleaching powder solution containing N/200 available chlorine. The effect upon the sample in comparison with the standard is noted after 15 minutes, 1 hour, and 24 hours at room temperature. The sample should show no greater loss than the standard.

The copying properties of the ink are determined by making press copies of the freshly made streaks of the ink under examination and of the standard. The original streaks and the copies are exposed to light and reagents as prescribed in the preceding paragraphs.

The content of metallic iron may be determined by any suitable chemical procedure. Total solids, ash, and iron can be determined on the same sample.

Evaporate 10 cc of ink to dryness in a porcelain dish on the steam bath, heat in the oven at 100° C. for one hour, cool in a desiccator and weigh. Report as total solids per 100 cc.

Burn the residue from the determination of total solids at the temperature of low redness. Too high a temperature will cause the iron oxide to become insoluble in hydrochloric acid. Cool in a desiccator and weigh. Report as ash per 100 cc.

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. Dilute to 400 cc, filter if necessary, 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. The iron is calculated as grams per 100 cc.

In case a number of samples are to be analyzed at one time it is suggested that the following method be used for the determination of iron:

After dissolving the ash in hydrochloric acid, add about 5 cc of concentrated sulphuric acid and evaporate in the hood until fumes of sulphuric acid escape. Dilute with 100 cc of water, heat to dissolve the ferric sulphate, filter, wash through a Jones reductor, and titrate with standard potassium permanganate. The iron is calculated to grams per 100 cc.

The keeping qualities of ink are very important. Some samples show very little decomposition at the end of a year; others deposit so much sediment and form so much scum that they are unfit for use at the end of a week. Twenty-five cc each of the sample and of the standard are allowed to stand undisturbed in similar colorless glass vessels loosely covered with filter paper to keep out dust. After two weeks' exposure to diffused daylight and air at ordinary room temperature the sample should be as free from mold and deposit upon its surface and upon the sides and bottom of the container as the standard.

The corrosive action of ink on steel pens may be determined in the following way: For each sample under test, including the standard, two new pens are selected from the same box. It has been found that pens from different boxes may vary so much that comparable results can not be obtained. Clean the pens with alcohol and ether to remove the film of grease, dry them in an oven at 105° C., and weigh each pair to the nearest milligram. Immerse each pair of pens in 25 cc of the ink contained in a small beaker or flask. After 48 hours remove the pens, wash and scrub them with water and a cloth to cleanse them thoroughly, rinse them with alcohol, dry them in an oven, and weigh. If the pens in the sample ink lose more weight than those in the standard, two more tests should be made. If the loss in one of these tests is greater than the loss in the standard ink, it indicates that the acid content of the sample is higher than that of the standard.

There are several other determinations of an analytical character which are indicative of the composition of the ink, but tell little concerning its quality.

Sulphuric anhydride is determined as follows: To 10 cc of the 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 the oven at 120° C. Ignite at as low a temperature as possible and cool, then place the dish in a 600 cc beaker, cover with distilled water containing 5 cc of bromine water, and heat for one hour on the steam bath, to oxidize to sulphate any lower compounds of sulphur which may have been formed in the ignition. Filter, render slightly acid with hydrochloric acid, boil off the bromine, add 10 cc of 10 per cent barium chloride solution, and let stand overnight. A blank determination should be run as a check on the reagents. Filter, wash, ignite, and weigh. Calculate to grams of SO_3 per liter.

Tannin can be determined in the following way: Place 10 cc 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 all the tannin is removed by the ethyl acetate. This will require about two hours. Remove the solution and shake it out three times with a half-saturated solution of potassium chloride to remove any iron salts present. Evaporate the solution, take up the residue with a little water, filter if necessary, evaporate in a tared dish, dry in an oven at 105° C., and weigh. Any other suitable continuous extraction apparatus can be used.

There are a few qualitative tests which are helpful in identifying the ingredients in blue-black inks.

The temporary color of the ink is usually a synthetic dye, but Prussian blue and logwood are sometimes used. As a rule it is not necessary to identify the coloring matter, but if it is desired the following general procedure should be followed: By suitable tests the class of dyes to which the color belongs is determined. Since only those dyes can be used which are not precipitated by tannin or acid, whole classes are thereby excluded from consideration. When the class has been determined, further special tests are made to ascertain the particular dye. For details of the testing, one of the larger books on dyes should be consulted.

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

It is difficult to test for the presence of gum and dextrin. Glycerol is detected by treating the total solids of the ink with alcohol. The alcohol extract is evaporated and the residue tested for glycerol, which gives off fumes of acrolein when heated with potassium bisulphate.

2. TESTING OF CARBON INKS

Carbon inks are used most extensively as drawing inks. The following method for the testing of waterproof drawing ink can be modified to suit the examination of carbon writing inks. Practical tests of the physical properties show more concerning the quality of the ink than a chemical analysis. The following method is suggested:

After standing two weeks in a closed container there should be no deposit on the sides or bottom of the container.

Marks are made on tracing cloth and drawing paper in the usual way with a drawing pen so regulated that the mark is approximately one sixty-fourth of an inch in width. The ink should flow freely and smoothly from the pen.

Ten minutes after the marks have been made they are rubbed gently with the finger tips. There should be no blurring or smudging.

When the marks have been allowed to dry for one hour they are examined for color and opacity. The color should be an intense black and the marks absolutely opaque when the tracing cloth is held close to a bright light.

The paper and tracing cloth are cut into inch-wide strips at right angles to the marks. Some of the strips are kept away from light and fumes and others used for making the following tests:

After exposure to direct sunlight for 96 hours or at a distance of about 10 inches from an arc or ultra-violet light for 48 hours, the marks should show no fading.

Strips of the drawing paper are soaked in water, gasoline, benzene, and carbon tetrachloride for 15 minutes at room temperature. The marks should show no running or smearing. The organic solvents are used in cleaning drawings. It is therefore desirable to have an ink which is not only waterproof but which is not affected by these solvents.

Five cc of the sample in a 50-cc beaker is inoculated with spores of the common green mold, and then kept in a moist chamber for two weeks at laboratory temperature. At the end of that time the ink should show no growth of mold, no thickening, and no separation of the pigment.

3. TESTING OF DYESTUFF INKS

The following procedure for testing red ink is typical of the method for the examination of dyestuff inks. The tests are practical, as the quality of the ink is judged by its performance rather than by the ingredients of which it is composed.

The ink under examination is tested in comparison with a standard made according to the formula on page 11.

Streaks are made in the manner described on page 18 under the testing of iron gallotannate inks.

When the streaks are dry, the sheet is examined on the front and the reverse sides. The streaks should have the same general form as those of the standard. They should be as uniform in color when viewed from the front and the back, and should show no more evidence of striking through the paper.

The paper is cut into inch-wide strips at right angles to the streaks. Some of the strips are kept away from light and fumes, and others are used for making the following test after the ink has been allowed to dry for one hour.

The strips are exposed to direct sunlight for 48 hours, or at a distance of about 10 inches from an arc or ultra-violet light for 24 hours. The streaks of the sample should show no more evidence of fading than those of the standard.

4. TESTING OF HECTOGRAPH INKS

The practical test is the only one of value in the examination of hectograph inks. Writing is made with the ink and transferred to the hectograph by pressing the paper on the surface and leaving it in contact for one minute before removing it. As many legible copies as possible are made by pressing fresh sheets of paper gently with the finger tips or a roller upon the hectograph surface, and allowing them to remain in contact for 10 seconds before removing them. The character of the impressions, whether sharp or blurred, and the number of copies obtained are considered in judging the quality of the ink.

5. TESTING OF INDELIBLE INKS

The composition of indelible marking ink is of subsidiary importance in comparison with the results of practical test. The following procedure is suggested:

Test specimens are prepared by writing with the ink on any closely woven fabric, either cotton or wool, in the exact manner prescribed in the manufacturer's directions accompanying the sample.

The marks should be clear and distinct, and there should be no discoloration beyond the limits of the marks after standing two weeks.

A large use for indelible inks is found in marking articles sent to commercial power laundries. The ink must withstand the effects of detergents, such as soap and soda; of "sours," such as oxalic acid, acetic acid, and sodium bisulphite, which are employed to neutralize any alkali; and of bleaching solution. In the laboratory tests it is required that the marks shall be still clearly legible after washing six times with each of the following solutions:

The soap solution contains 7 g of pure soap and 7 g of modified soda (58 per cent sodium carbonate and 42 per cent sodium bicarbonate) in 1 liter of distilled water. The test specimens are immersed in the solution at 65 to 71° C. (149 to 160° F.) for 15 minutes. They are then rinsed five times in distilled water and dried. The entire procedure is performed six times.

The oxalic acid solution contains 6 g of crystallized oxalic acid dissolved in 1 liter of 28 per cent acetic acid. The test specimens are immersed in the solution at 65 to 71° C. (149 to 160° F.) for 10 minutes and treated as described for the soap solution.

The sodium bisulphite solution contains 5 g of sodium bisulphite and 72 cc of hydrochloric acid, 21.9 per cent (sp. gr. 1.11), in 1 liter of distilled water. The test specimens are immersed at 65 to 71° C. (149 to 160° F.) for five minutes and treated as described for the soap solution.

The bleaching solution contains 1/100 per cent of available chlorine. The test specimens are immersed at 65 to 71° C. (149 to 160° F.) for five minutes and treated as described for the soap solution.

Further test specimens for the determination of the effect of the ink on the breaking strength of cotton and wool are prepared as follows:

Strips 4 inches wide and 36 inches long are cut in both the warp and filling directions from a suitable, closely woven fabric, either cotton or wool. Each strip is cut into six test specimens 6 inches long. Three specimens of each strip are left untreated; to the remaining three the ink is applied across the width at the center in a streak approximately 1 inch wide. The breaking strength of the untreated fabric, and of the treated fabric 10 days after being marked, is determined by the standard grab method. The breaking strength of the treated fabric should be not less than 90 per cent of the breaking strength of the untreated fabric.

6. TESTING FOR INVISIBLE WRITING

When it is suspected that an apparently innocent letter carries a secret message, that may have a criminal intent or may convey information to the enemy, the investigator must proceed cautiously in order to bring out the writing without destroying the evidence. To that end he must have a good general knowledge of the substances that are used for secret writing, so that he can employ at first the most likely and least harmful means of making it visible, and after that more drastic treatment if necessary.

Because of the many substances that may be used, no general scheme for the examination can be given, but only a few suggestions. The first treatment would be to heat the paper gently, because this will bring out writing with milk, sal ammoniac, or acids. It will dehydrate the nearly or quite invisible pink writing with cobalt chloride solution and change it to a conspicuous blue. If heating does not develop any writing, several spots on the paper may be fumed with hydrogen sulphide or moistened with ammonium sulphide applied with a feather or a thin stirring rod.

In like manner other chemicals can be applied until the right one to use is found, or until it is certain that there is no invisible writing.

7. RESTORATION OF FADED WRITING

The deciphering of writing that has faded out from age presents a problem that is in some respects similar to the detection of invisible writing. There is little hope of restoring writing made with inks that are solutions of dyes, because practically nothing is left on the paper when the color has disappeared. If the ink contained iron gallotannate, there will always be some brown oxide of iron left on the fibers of the paper, and this can be changed into a more intensely colored iron compound. The simplest treatment is to expose the paper to the fumes of ammonium sulphide, which will change the iron oxide into black iron sulphide. Another method is to apply a solution of tannin, which will form black iron gallotannate.

When it was decided to exhibit the Declaration of Independence in the Library of Congress, the suggestion was made that the writing should be restored with chemicals. Owing to the danger of damaging the document irreparably during the treatment, and because of the possible aftereffects of the chemicals upon the paper, this was not done.

Writing that has been obliterated by the action of chemicals can sometimes be restored by judicious treatment with suitable reagents if enough iron or other metal is left in the paper. Sometimes photographs will bring out contrasts in color that are not perceptible to the eye, and will thus make the writing legible. Still another method of examination is to allow ultra-violet rays to fall upon the paper in a dark room. The writing will become more intensely fluorescent than the rest of the paper and can be read.[5]

Sometimes when papers are charred by fire, the writing is still visible because of a difference in luster of the parts where the ash of the ink remains. It may be possible with an iron ink to convert the iron oxide in its ash into soluble iron chloride; then by making a press copy on paper moistened with potassium ferrocyanide to bring out the writing as lines of Prussian blue. In one interesting case where all other means failed, the writing was successfully transferred to photographic plates, between which the charred paper was kept for one or two weeks. Apparently gases which emanated from the charred paper fogged the plates except where the remains of the writing and printing acted as a screen to prevent their escape. Excellent negatives were obtained when the plates were developed.[6]

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[5] Fonzes-Diacon, Faucon and Reynaud, Ann. falsifications, **17**, pp. 20–23; 1924.

[6] R. Davis, B. S. Sci. Papers, **18** (No. 454), p. 447; 1922.

8. TESTING OF STAMP-PAD INKS

Since the base of most stamp-pad inks is glycerol, which is hygroscopic, the container should be kept open only long enough to remove the portions needed for testing.

Equal volumes of the ink under examination and of a standard ink of the same color, prepared according to the formula on page 13 are spread on equal areas of a new stamp pad. If a large number of samples are to be tested, the following substitute for commercial pads will be found useful: Two shallow brass rings, about 1½ inches in diameter, are cut from two pieces of brass tubing. The tubing must be of such size that the larger ring will fit over the smaller one just tightly enough to hold taut a piece of thin muslin. Pieces of white felt are cut to fit snugly inside of the inner ring and form the base of the pad. They are easily cut by means of a die made by sharpening one end of a short length of brass tubing. The inner ring is filled level with disks of felt; a larger circle of thin muslin is laid over them and stretched by pressing the outer ring into place. The pad so prepared is placed on a glass plate or other nonabsorbent surface. The measured amount of ink is then applied from a pipette, which can be made from glass tubing and calibrated with sufficient accuracy with little trouble. It is convenient to have a number of pipettes and of sets of rings marked in series. At the completion of the test, the felt and muslin are discarded.

Impressions are made with a clean rubber stamp upon white bond paper. The impressions are examined when fresh, and the time required for drying is noted. The sample should take no longer to dry than the standard, and should give as sharp and intensely colored impressions.

The pads are exposed to atmospheric conditions for 10 days and the tests are then repeated. During this time the sample should show no more evidence of excessive hygroscopicity or of drying and caking on the pad than the standard.

The effect of light on the ink is determined by covering with black paper one-half of the sheet on which the impressions have been made. The sheet is then exposed to direct sunlight for 48 hours, or at a distance of about 10 inches from an arc or ultra-violet light for 24 hours. The sample should show no more evidence of fading than the standard.

The specific gravity of the ink can be determined by means of a picnometer or a hydrometer at 20° C. and referred to water at the same temperature.

9. ANALYSIS AND TESTING OF RECORDING INKS

The specific gravity is determined by means of a hydrometer at 20° C. and referred to water at the same temperature. This gives an indication of the amount of glycerol present. The insoluble matter is determined by filtering through ordinary qualitative filter paper and washing with hot water. The ink should contain no insoluble matter. Writing made with the ink should show no tendency to blur on rosin-sized paper.

10. ANALYSIS AND TESTING OF CANCELING INKS

Since canceling inks contain more or less insoluble and volatile matter, special attention must be given to sampling, the ink must be thoroughly mixed by shaking or stirring before any is removed, and the container should be kept open only long enough to remove the portions necessary for analysis.

There are several determinations which are of value if a very thorough examination of the ink is to be made, but which need not be carried out in ordinary testing. They are described in detail in the Bureau of Standards Miscellaneous Publication No. 15. Methods are given for determining the amount of ingredients volatile at ordinary temperatures, for following the course of diffusion of the dye and the rate of penetration of the carbon by absorption in strips of blotting paper.

The amount of carbon is ascertained as an indication of the permanence of the ink. The ash determination shows whether inorganic materials are present in addition to the carbon. The practical tests give the best indication of the quality of the ink.

For the determination of the amount of carbon, weigh about 2 g of ink in a small beaker and dilute with a suitable solvent. Filter through a Gooch crucible containing a thin asbestos pad, and wash with the solvent until all the oil and soluble color are removed. Alcohol is used as the solvent for rosin and castor oils; ether, benzene, or petroleum ether for other oils. Often the carbon is in such a finely divided state that it is carried through the asbestos pad with the solvent. It has been found that the addition of a few cubic centimeters of ether to the ink before the addition of alcohol or other solvent tends to agglomerate the carbon so that the solution can be more readily filtered. The Gooch crucible is finally washed with alcohol and ether and dried in the oven at 105° C. It is then ignited in a muffle, or over a low flame, cooled, and weighed. The loss in weight is reported as carbon. The result will be slightly in error if Prussian blue toner or other decomposable metallic compound is present. The lampblack prepared for the manufacture of canceling ink should yield less than 0.5 per cent of ash.

The practical tests are carried out as follows: A measured amount of ink is applied to a new stamp pad as described under the testing of stamp pad inks on page 26. Impressions are made with a clean, metal stamp on white bond paper. The impressions are examined when fresh and the time required for drying is noted. The ink should dry rapidly and give sharp, intensely black impressions with no tendency to form an oily zone. After drying the impressions are exposed to the following reagents: Water, water with the addition of 10 per cent of strong ammonia (sp. gr. 0.90), 95 per cent alcohol denatured with methanol, alcohol with the addition of 10 per cent of strong ammonia, 2 per cent hydrochloric acid, and bleaching solution containing N/200 available chlorine. Each impression is exposed in a small Erlenmeyer flask to about 50 cc of the reagent for 24 hours. Its appearance is noted at the end of 15 minutes, 1 hour, and 24 hours.

For the light test other impressions are exposed to direct sunlight for 96 hours or at a distance of about 10 inches from an arc or ultra-violet light for 48 hours. The tests with reagents are considered of less value than the light tests and are not always applied.

11. TESTING OF TYPEWRITER AND OTHER RIBBONS

The fabric is examined according to the following methods:

Visual examination is made of the sample to determine the nature of the edge and the character of the cloth in respect to its freedom from waste and avoidable imperfections of manufacture, and to ascertain if the cotton had been combed. It is first necessary to remove the ink by soaking in an organic solvent, such as benzene or chloroform.

The actual number of threads in 1 inch is counted in the filling direction at three different places and the results averaged. The total number of warp threads is counted and calculated to the basis of 1 inch.

It is rarely necessary to determine the breaking strength of typewriter ribbons, but it is desirable to know the strength of ribbons used on computing and recording machines. It is determined in the following way: Three test specimens approximately 6 inches long are cut, one from each of the ends and one from the middle of the ribbon. If the ribbon is wider than 1 inch, each specimen is raveled to exactly 1 inch in width by taking from each side approximately the same number of threads. If the ribbon is narrower than 1 inch the results of the breaking strength are calculated to the basis of 1 inch width.

The width is determined by laying the material on a flat surface without tension, then measuring the distance perpendicular to the length between the edges. Three measurements are taken at different places on the sample and the results averaged.

The appearance of the writing and the serviceability are determined by testing on a typewriter or suitable automatic testing machine. An automatic testing machine makes it possible to eliminate such errors as variations in touch, but these machines do not always reproduce the actual conditions of use in a typewriter.

If the ribbon to be tested is wound on a spool that will not fit the machine used for testing, it must be transferred to a suitable spool. The ribbon is placed in the machine and two yards of its free end are wound upon the empty spool. This is done so that the ribbon will shift a definite distance while making the following tests. The amount that the ribbon shifts is controlled by the amount already on the spool. If the circumference of the coil of ribbon already wound on the spool is large, the ribbon moves a correspondingly greater distance than if the circumference is small. For this reason the ribbon must be reeled back to the starting point at the end of each line. The starting point can be easily indicated by making a pencil mark at the point where it leaves the spool holder. With some machines it is possible to prevent the travel of the ribbon by raising the ribbon-feed pawl. The latter method is preferable when possible.

A sentence about 30 letters in length is written 25 times. At the beginning of each line the ribbon is reeled back to the starting point. The first line should be clear and clean with no blurring of the letters. The writing becomes fainter as the ink is exhausted, but the twenty-fifth line should be distinct and easy to read. To determine recovery, the ribbon is allowed to stand at rest for one hour, after which another line is written. This gives the ink time to travel from the fresh portions to the part from which it has been exhausted. This line should be as clear and distinct as the third line of the preceding 25.

The writing produced by this test is half covered with black paper and exposed to sunlight, arc, or ultra-violet light. Writing made with colored ribbons, or press copies therefrom, after exposure in a similar way to direct sunlight for 48 hours, or at a distance of about 10 inches from an arc or ultra-violet light for 24 hours, should still be easily legible.

The small letter "e" is thoroughly cleaned and 800 impressions made with it with the normal feed of the ribbon. There should be no evidence of filling of the type.

Hectograph ribbons are tested in the same way. The writing produced as described above is transferred to a hectograph pad and 25 copies made from it in the usual way. All of the copies of the first line of writing should be easily legible.

Computing and recording machine ribbons are tested as described above with a few changes. The figures 0 to 9 are written 50 times, the ribbon is allowed to rest for one hour, and another line is written. This line should be as distinct and legible as the fifth line.

The figure 8 is used for the type-filling test and 200 impressions are made with it.

12. TESTING OF CARBON PAPER

The weight and composition of the tissue are determined after the carbon has been removed by soaking in a suitable organic solvent, such as benzene, chloroform, or carbon tetrachloride. The carbon can be removed conveniently by fastening the paper to a roll, which slides into a box, where it is revolved with its surface against a piece of felt in a bath of vaporized benzene.

The weight is expressed in pounds per Government standard ream of 500 sheets, 25 by 40 inches in size, and also in the trade custom ream of 500 sheets, 20 by 30 inches in size. Five sheets are accurately measured to 1/20 inch. If the paper is coated, the coating is removed after measuring. After two hours in the conditioning room, which has a temperature of 70° C. and relative humidity of 65 per cent, the five sheets are weighed together on a chemical balance. The following formula gives the method of calculation:

$$\frac{\text{Weight in grams} \times 1.102 \times 200}{\text{area of 1 sheet in square inches}} = \text{Weight in pounds per ream of 500 sheets, 25 by 40 inches.}$$

To convert this weight to the trade custom size of 20 by 30 inches, multiply by 0.6.

The kinds of fiber in the paper and the proportions of each are determined by the usual microscopical methods. A complete description of these methods is given in Bureau of Standards Circular No. 107, The Testing of Paper.

There are three qualities to be considered in testing the writing qualities of carbon paper: The general appearance, the serviceability, and the manifolding properties.

The coated paper is examined to determine whether the coating has been evenly and uniformly applied. The presence of pinholes or other imperfections is noted. The paper should lie flat on a smooth surface for ease in handling by the operator.

The most reliable test of the serviceability of a sample of carbon paper is its performance in actual use. The Government specification requires a carbon paper to be so well coated as to make not less than 50 clean, clear, legible first copies when a No. 16, 50 per cent rag bond paper first sheet and a No. 9 manifold bond copy sheet are used. It is a long, tedious process to exhaust the carbon in this way if many samples are to be tested at one time. There are automatic devices for testing carbon paper by holding the paper in a fixed position and exhausting the ink by writing repeatedly on the same place. The automatic testing machine eliminates the errors due to variation in touch of the operator, but does not always reproduce the action of the blow from a typewriter key, and it is difficult to regulate the tension of the test specimens as they are held in a fixed position. A laboratory method suitable for any typewriter and which gives comparative results is as follows:

No. 16, 50 per cent rag bond paper is used for the first and second sheets. A piece, approximately 1 inch square, of the carbon paper under examination is fastened with paper stickers to the first sheet so that the coated side will come in contact with the second sheet in the usual way. The first sheet is fastened securely with pins to the bar back of the platen or in any other suitable way so that it remains stationary while the second sheet moves freely with the platen as it rotates in spacing. In this way the same letters can be written repeatedly on the same portion of the carbon paper until the coating is exhausted. Since the second sheet moves as the platen is shifted the course of the fading of the carbon can be followed. The writing on the first line should be clear and distinct and show no tendency to rub or smut.

The manifolding properties are of importance only in testing the lightweight papers which are intended for making a large number of copies at once. The number of manifold copies obtainable depends upon the character of the carbon paper, upon the weight and finish of the paper used for the first sheet and for the manifold copy sheets, upon the hardness of the platen, and upon the stroke of the typewriter, and the typist. The results, therefore, are only comparative. The Government specification divides carbon papers into two classes, as follows:

The first class is required to make not less than 5 clean, clear, legible carbon copies at a time, using a No. 16, 50 per cent rag bond first sheet and No. 9, 50 per cent rag bond manifold copy sheets.

The second class must make not less than 10 clean, clear, legible carbon copies at one time, using a No. 16, 50 per cent rag bond first sheet and No. 7, 50 per cent rag bond manifold copy sheets.

It must be remembered in testing carbon papers that the results are only comparative. Only papers of the same general weight and finish can be compared. A lightweight paper will fail in the serviceability test long before a heavier paper, but it will give a greater number of manifold copies. The purpose for which the carbon paper is intended must be considered in estimating its quality.

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