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DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
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Letter
Circular LC 331

(Superseding
Circular No.95)

INKS

This letter circular is for the benefit of the numerous correspondents who ask how to make various kinds of inks. In it are given the formulas for the standard inks in several Federal specifications, and selected formulas of inks for which there are no specifications.

Methods of testing are omitted, because the average user of ink is perfectly satisfied if it has a good color and works well. Those who wish to test inks can buy copies of the specifications. See last page.

Manufacturers and others frequently misunderstand the purpose of the formulas for the standard inks in the specifications. It is not required that inks supplied to the Government shall be made strictly according to the formulas, but only that the inks so supplied shall be equal to the standard inks in every essential quality. This applies especially to the first two of the inks, because the materials used in their formulas must be of the purity established by the United States Pharmacopoeia. By suitable chemical control of his manufacturing processes, anyone who can make ink from cheaper raw materials is at liberty to do so and may sell his product to the Government, if it is as good as the standard ink. Of necessity the materials used in the standard inks must be of the same purity, so that both seller and buyer will know exactly what is wanted.

Weights and Measures.

In some of the formulas the ingredients are in "parts by weight". By choosing an appropriate unit it is evident that the formulas can be used for making the inks in any quantities desired. In most of the formulas metric units are used, and lest the unaccustomed reader should be discouraged at the outset, a few conversion factors are given.

1 gram equals 15.43 grains, or 0.0353 oz. avoir.
1 oz. avoir. equals 28.35 grams
1 lb. avoir. equals 453.6 grams
1 liter equals 1.0567 U.S. liquid quarts
1 milliliter equals 0.0338 liquid oz. (The milliliter is commonly but wrongly called cubic centimeter)
1 U.S. liquid gallon equals 3.785 liters
1 U.S. liquid oz. equals 29.57 milliliters
1 gram per liter equals 0.1335 oz. avoir., or 58.4 grains, per U.S. liquid gallon.

For all practical purposes, a milliliter of water weighs 1 gram. By definition, this is exactly true at 4°C (39.2°F). Other liquids weigh more or less, in proportion to their densities. Required weights of liquids can be converted into volumes if their densities are known. Thus, if the density of the liquid is 1.30, that of water being 1.00, a given weight, say 100 grams, of the liquid will have a volume of 100/1.30, or 76.9 milliliters. This holds for only one temperature, strictly speaking, but it is accurate enough for the present purpose , at other temperatures.

Ink: Copying and Record. Federal Specification TT-I-521.

All the ingredients in the standard ink must be of the quality prescribed in the current edition of the United States Pharmacopoeia.

Tannic acid	23.4 grams
Gallic acid crystals	7.7 "
Ferrous sulphate	30.0 "
Hydrochloric acid, dilute . . .	25.0 "
Phenol (carbolic acid)	1.0 "
Soluble blue	3.5 "
Water to make 1 liter at 20°C (68°F)	

Here as in all other formulas, "water" means distilled water, if it can be had. Rain water is second choice.

Dilute hydrochloric acid, U.S.P., is of 10 per cent strength. Concentrated hydrochloric acid as commonly sold is a water solution containing about 36 per cent by weight of hydrochloric acid gas, so as to make the 10 per cent acid, 100 parts by weight of concentrated acid must be diluted with 260 parts by weight of water.

Soluble blue is one of the comparatively few dyes that are not precipitated by the other ingredients of the ink. When buying a supply of it, be careful to say that it is to be used for making ink. See the list of dyes on a later page of this letter.

To make the ink, dissolve the tannic and gallic acids in about 400 milliliters of water at a temperature of about 50°C (122°F). Dissolve the ferrous sulphate in about 200 milliliters of warm water to which has been added the required amount of hydrochloric acid. In another 200 milliliters of warm water dissolve the dye. Mix the three solutions and add the phenol. Rinse each of the vessels in which the solutions were made with a small quantity of water, and use the rinsings to make the volume of ink up to 1 liter at room temperature. Be sure the ink is well mixed before it is bottled. If sealed hermetically in a glass bulb, the ink will keep for years with practically no formation of sediment. So when bottling the ink, have good tight corks and fill the bottles almost to the corks.

This ink is primarily for records, and is not like most copying inks. However it will make one good press copy when the writing is fresh, and this will generally suffice.

<u>Ink: Writing</u>. Federal Specification TT-I-563.

Except for the phenol and dye, this ink is half as concentrated as the record and copying ink. It is similar to some of the commercial writing fluids and fountain pen inks. The standard is made in the same way as the preceding ink, and from materials of the same quality. If made with slightly more hydrochloric acid than the formula calls for it will keep longer without depositing sediment, but it will be more corrosive to steel pens.

The standard formula is:

Tannic acid	11.7	grams
Gallic acid crystals	3.8	"
Ferrous sulphate	15.0	"
Hydrochloric acid, dilute	12.5	"
Phenol (carbolic acid)	1.0	"
Soluble blue	3.5	"
Water to make 1 liter at 20°C (68°F)		

Concentrated Ink, Powder and Tablets. Federal Specification TT-I-56

Concentrated ink that meets all the requirements of the specification can be made by cutting down the amount of water to a minimum, so as to make a pasty mass or a thick fluid with the solids only partly dissolved. Instead of hydrochloric acid, which is volatile, an equivalent quantity of sulphuric acid is used; that is, 1.77 grams of the usual concentrated acid of 95 per cent strength (66 deg. Baumé).

Ink powders and tablets were included when the specification was written, though all that had been examined up to that time were either a dye, for instance nigrosine, or wholly unsatisfactory mixtures purporting to make good iron gallo-tannate ink when dissolved in water. A few months before this letter circular was written, one manufacturer succeeded in making an ink powder that meets all the requirements. This Bureau is not able to say how this powder is made.

Ink: Red. Federal Specification TT-I-549.

The standard ink is made by dissolving 5.5 grams of crocein scarlet 3B in 1 liter of water.

Other Colored Inks.

There are no Federal specifications for inks of other colors than red. Any water-soluble dye dissolved in water can be used as ink, though not all dyes are equally suitable for the purpose. It is useless to give a general formula for the amount of dye to dissolve in a given volume of water, because of the great differences in tinting strength. With some dyes more, and with others less than the 5.5 grams per liter specified for crocein scarlet, would be required. If the quantity of dye available is small, make a concentrated solution and dilute it by degrees until it writes with a satisfactory depth of color. It is not safe to depend upon its appearance in the bottle. Many dyes have an antiseptic action, but solutions of others will become moldy, and it is necessary to prevent this by means of phenol or some other preservative. One gram per liter is enough. In case the ink shows a tendency to blur or "feather" on good writing paper, dissolve 1 or 2 per cent of gum arabic in it.

As already said, most ink powders and tablets consist of water-soluble nigrosine. A much more attractive color is naphthol blue-black, though it is not as permanent as nigrosine.

Acid-Proof Inks.

The few samples of acid-proof inks received for test during the course of many years were either solutions of prussian blue alone, or they contained in addition a dye to make their color darker. They were labeled "blue-black", though that term should be reserved for the iron gallo-tannate inks that write blue, and turn black on paper.

The usual form of prussian blue is not soluble in water, and it is technically difficult to make the variety called soluble prussian blue. Fortunately the pigment can be gotten into solution by mixing it with one-fifth or less of its weight of crystallized oxalic acid. As some of the blue may not dissolve, it is a good idea to make the solution with less water than the formula calls for, and then to dilute it as much as seems desirable. From 40 to 50 grams of prussian blue will probably be required with 1 liter of water. Some of the few published formulas call for amounts of oxalic acid up to one-half the weight of the prussian blue, but we have found one-fifth to be ample.

Prussian blue ink resists attack by some acids, but alkaline solutions decompose it and leave a rusty stain of iron oxide. Ink eradicators of the acid-Javelle water type will remove it, though not easily.

Hectograph Ink.

Years before some of the modern duplicating devices had been invented, the hectograph was used for printing small editions of circular letters, etc., and it is still in rather wide use. The original is written with a special ink that contains a large proportion of a dye that has good tinting strength. The letter is then pressed face-downward upon a gelatin-glycerin or a clay-glycerin pad, which absorbs a considerable amount of the ink. From this pad it is possible to print a number of increasingly paler copies upon other sheets of paper. The name, hectograph, "hundred writing", exaggerates somewhat, unless copies so pale as to be barely legible are counted. In experimenting with quite a number of dyes, it was found that the following would give at least 30 copies with unbroken lines, and numerous other copies that were easily legible, though there were breaks in the strokes of the pen. Methyl violet gave the most copies, the best red dye was rhodamine B, and emerald green and Victoria blue were the best of their colors.

The ink used in making these tests was prepared according to the formula:

Acetone	8
Glycerin	20
Acetic acid, coml. 30%	10
Water	50
Dextrin	2
Dye	10

All parts are by weight. If the unit chosen is 1 gram, the formula will make about 90 milliliters of ink.

Stamp-Pad Ink. Federal Specification TT-I-556.

A solution of dye in water could be used on a stamp pad, but it would soon dry out. A mixture of equal volumes of glycerin and water remains moist under all atmospheric humidities, though the water content of the mixture fluctuates. In each 100 milliliters of the mixture of glycerin and water dissolve 5 grams of dye. The following are used for making the standards of different colors in the specification: water-soluble nigrosine (black), soluble blue, light green, magenta (red), and acid violet.

Recording Inks.

There is no Federal specification for recording ink. For outdoor recording instruments the Weather Bureau uses inks made by dissolving about 10 grams of dye in 1 liter of a mixture of equal volumes of glycerin and water. As this mixture will freeze in some parts of the country, it is sometimes necessary to add a certain proportion of alcohol to the ink.

For recording instruments in the laboratory, the ink needs to contain only enough glycerin to prevent its drying at the tip of the pen. A mixture of 1 volume of glycerin and 3 volumes of water has been found satisfactory.

Almost any water-soluble dye might be used were it not that some of them rather unaccountably make blurred lines on the usual card and paper charts. Dyes that have been found to work well are crocein scarlet, fast crimson, brilliant yellow, emerald green, soluble blue, methylene blue, methyl violet, Bismarck brown, and water-soluble nigrosine.

Indelible Marking Ink. Federal Specification TT-I-542.

No formula for a standard marking ink is given in this specification. Of the numerous formulas in books, those containing a silver salt, and others designed to produce aniline black on and in the fibers, are most common. A typical formula of each kind is here given.

Dissolve 5 grams of silver nitrate in its own weight of water, and add ammonia water (not household ammonia) until the precipitate that first forms just dissolves. Separately dissolve 5 grams of gum arabic in 10 milliliters of warm water, and 3 grams of anhydrous sodium carbonate (or 3.5 grams of the monohydrate) in 15 milliliters of warm water. Mix the three solutions and warm until the mixture starts to darken. This ink should be used with a gold or a quill pen if possible, but if not, with a clean steel pen. The writing should be exposed to direct sunlight or pressed with a hot iron to develop the color. The ink must be kept in the dark.

Aniline black inks are made in one or in two solutions, the argument for the latter being that the chemical reaction that produces the color must take place largely in the fibers where the mark is wanted. There is no chance for the color to be formed in the bottle before the ink is applied to the fabric, and to make a sediment that can not penetrate into the fibers. However, excellent one-solution inks can be bought.

For a two-solution ink the following has been recommended:

Solution A.-

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

Solution B.-

Gum arabic	67
Water	335
Aniline hydrochloride	200

Keep in separate bottles. Immediately before use mix 1 volume of A and 4 volumes of B.

Drawing Inks.

There is at present no Federal specification for drawing ink. The commercial black drawing inks are suspensions of carbon in a water solution that contains substances which keep the particles of carbon from settling to the bottom, and which usually make the marks on paper or tracing cloth waterproof when they once become dry. Shellac dissolved in a dilute solution of borax, or of borax and ammonia, is believed to be the usual waterproofing agent, and it also acts as a "protective colloid" to keep the carbon in suspension. Success in making carbon inks seems to depend partly upon long-continued grinding in a ball-mill.

Comparatively few colored drawing inks are made with pigments, but are clear solutions of dyes. Most of them are called waterproof, but all that we have examined "bled" a little when lines drawn with them were kept under slight pressure in contact with a piece of wet paper. This is a very severe test. As it is not practicable to make waterproof colored inks in the home, the process need not be described.

Sympathetic or Invisible Inks.

It would be absurd to write a specification for ink that is intended for secret messages or records. The greatest variety of substances can be used for ink of this kind, and some of them have been known and used for many centuries. The following materials, found in every home, are potential sympathetic inks: alum, soda (baking and washing), borax, flour boiled with plenty of water, corn sirup thinned with water, soap, diluted mucilage, milk, lemon juice, and saliva. Some of these are very poor, indeed, but could be used if nothing better were at hand. Alum is by far the best, being about as good as a drop of sulphuric acid, for instance from a storage battery, mixed with ten or a dozen drops of water. Dilute sulphuric acid has been used for many years. The writing in all these cases is developed by pressing with a hot iron, or holding it above a gas flame so that the paper begins to turn brown.

Many invisible inks are developed by chemical treatment, preferably by fuming, but by the application of solutions when necessary. Thus, the vapors of ammonium sulphide will form brown or black sulphides of the metals, when the inks contain any of the following: iron (ferric) sulphate, mercuric chloride (corrosive sublimate), copper sulphate, cobalt chloride, nickel chloride and lead acetate. Some of these salts are colored, but the solutions can be so dilute as to be invisible on paper. Cobalt

chloride becomes deep blue in dry air or when heated moderately, and with strong heating the writing becomes permanently black. Ferric sulphate turns black with tannic acid, and blue with potassium ferrocyanide. The vapor from solid iodine turns starch ink blue. It will even bring out faintly writing done with distilled water on some kinds of paper, because the sizing is disturbed by the water, and this allows the paper to absorb more of the iodine vapor where it was wetted.

Special Inks.

Some of the books listed on a later page give formulas for making inks for writing on metals and other special surfaces. Most of the formulas have not been tried by us, and the inks are not used to any great extent, so it seems unnecessary to devote any space to them.

Pigment Inks.

Once a formula has been worked out for an ink that is composed of a mixture of liquids, or of solids dissolved in liquids, it is easy to duplicate the ink at any time; assuming of course that the ingredients are of the same purity as required by the formula. The situation is different if the ink consists of one or more pigments mixed with a fluid. In that case a formula simply gives an idea of how to make the ink, because the physical properties of the mixture depend largely upon how the materials are put together. The successful producer of pigment inks must have skill based upon experience. Besides black drawing ink and some with colored pigments, there are various kinds of printing inks, canceling, duplicating or mimeograph, and other kinds in this class.

Dyes for Ink Making.

There are many more names of dyes than there are kinds, because manufacturers like to have special names for their products. This readily leads to confusion in speaking or writing about dyes. To give an example: Bismarck brown, Manchester brown, phenylene brown, vesuvine, aniline brown, leather brown, cinnamon brown, canelle, English brown, golden brown, brown Y, and brown extra are names for the same dye, and this is not the worst case that could have been selected. To do away with this sort of confusion, two important compilations of dye names have been made. These are Schultz's Farbstofftabellen (dyestuff tables), and the Colour Index. In each of these books are brought together all the commercial names by which each dye type is known. Bismarck brown and

the other dyes just named have the same chemical composition and structure, and are therefore of the same type. In the books, each dye type is given a serial number, which therefore serves as a sort of specification for the type. Instead of saying Bismarck brown, the buyer could get it by asking for Colour Index No. 332 or Schultz No. 284.

Those who like variety can make writing and other inks of numerous colors and shades by using the dyes in the list. They are grouped according to Color, in the same order as in the spectrum, followed by brown and black.

	Col.Ind.	Schultz
Crocein scarlet MOO	252	227
Magenta (fuchsin)	677	512
Rhodamine B	749	573
Fast crimson	31	42
Diamine scarlet B	382	319
Orange II	151	145
Orange TA	374	311
Crocein orange	26	37
Metanil yellow	138	134
Phosphine	793	606
Auramine	655	493
Brilliant yellow	364	303
Emerald green	662	499
Light green SF	670	505
Guinea green B	666	502
Malachite green	657	495
Methylene blue	922	659
Victoria blue B	729	559
Soluble blue (see note below)	707	539
Naphthol blue-black S	246	217
Benzo blue 2B	406	337
Diamine sky blue FF	518	424
Benzo sky blue	520	426
Indigo carmine	1180	877

	Col.Ind.	Schultz
Methyl violet B	680	515
Crystal violet	681	516
Acid violet	698	530
Alkali violet	700	532
Benzamine brown 3GO	596	476
Bismarck brown R	332	284
Durol black B	307	265
Nigrosine, water-soluble	865	700

Note: A special effort may have to be made to obtain soluble blue that can be used in iron gallo-tannate ink without forming an insoluble precipitate with the iron or the tannic and gallic acids. Unless the blue is made "for ink", it may not be usable. One can always return to indigo carmine (sodium salt of sulphonated indigo), which was used before the days of synthetic dyes. Other dyes worth trying because they do not form precipitates, are naphthol blue-black S, benzo direct blue 2B, benzo sky blue, and diamine sky blue FF. They are not as bright in color as soluble blue, and they should not be adopted as substitutes for it without rigorous testing over a period of several months, in comparison with soluble blue that is known to be satisfactory.

In general it is advisable to buy dyes directly from the manufacturer, and to specify the concentrated form in each case. Many dyes are mixed with inert diluents before being put on the market. This is a recognized trade practice, and is not to be regarded as adulteration.

Bibliography.

There is probably no public library that does not have several of the books in the list below. Some of the books give formulas and little else, while others are concerned chiefly with the technical and scientific side of inks. Of the books listed, Nos. 1, 3, 5, 9 and 10 have appeared in more than one edition.

1. Brannt-Wahl, Techno-Chemical Receipt Book. H. C. Baird Company, New York, 1919.

2. Carvalho, Forty Centuries of Ink. Banks Law Publishing Company, New York, 1904.

3. Henley, Twentieth Century Book of Recipes, Formulas and Processes. Norman W. Henley Publishing Company, New York, 1928.

4. Lohner, Manufacture of Inks. Scott, Greenwood & Company, London, 1902.

5. Mitchell & Hepworth, Inks, Their Composition and Manufacture. Chas. Griffin & Company, London, 1924.

6. Rupert, Examination of Writing Inks, in Industrial & Engineering Chemistry, Vol. 15, p. 489; 1923.

7. Osborn, Questioned Documents. Lawyers' Co-operative Publishing Company, Rochester, N. Y. 1910.

8. Oyster, Spatula Ink Formulary. Spatula Publishing Company, Boston, 1912.

9. Scientific American Cyclopedia of Formulas. Munn & Company, Inc., New York, 1921.

10. Spon, Workshop Receipts. E. & F. Spon, London, 1917.

11. Underwood & Sullivan, Chemistry and Technology of Printing Inks. D. Van Nostrand Company, New York, 1915.

12. Wiborg, Printing Ink. Harper & Bros., New York, 1926.

Circular No. 95 of this Bureau is on Inks, Typewriter Ribbons and Carbon Paper. It is now out of print, but can be consulted in many libraries. It summarizes the several Federal specifications so that these need not be bought. However, if anybody desires to have them, they can be bought for 5 cents apiece from the Superintendent of Documents, Washington, D. C. Stamps will not be accepted in payment. The specifications are no longer issued as Circulars of the Bureau of Standards, and are now designated as follows:

TT-I-521, Ink; Copying and Record
TT-I-542, Ink; Marking, Indelible (for) Fabrics
TT-I-549, Ink; Red
TT-I-556, Ink; Stamp-Pad
TT-I-563, Ink; Writing

The journal, Chemical Abstracts, gives abstracts of articles on chemistry and related subjects that are published all over the world. It also cites patents issued in this and other countries. In the two decennial indexes, 1907 to 1916, and 1917 to 1926, and in the annual indexes since the last date, there are numerous entries relating to inks.