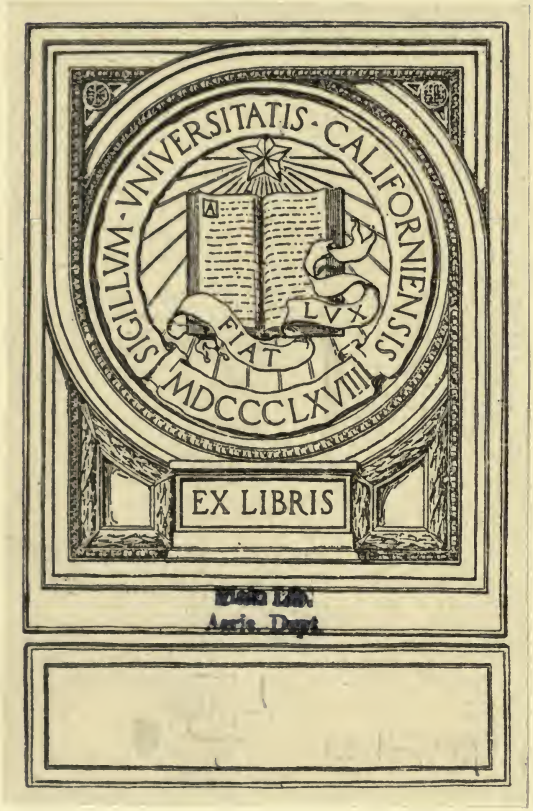

Circular No. 12, Revised.

United States Department of Agriculture,

BUREAU OF CHEMISTRY,

H. W. WILEY, Chief of Bureau.

METHODS FOR THE INVESTIGATION OF CANCELING INKS AND OTHER STAMPING INKS.

The following methods have been devised for the purpose of ascertaining the suitability of canceling inks for the use of the Post-Office Department. Many of these methods will be found of assistance in passing upon the quality of stamping inks for miscellaneous uses.

It is important that the ink used by the Post-Office Department for postmarking possess in the highest possible degree certain properties. The ink, first of all, must produce an indelible cancellation; that is, it must be relatively indelible as compared with the ink used for printing the postage stamps. The postmark made with the ink must dry quickly in order that the mail matter may be handled immediately without any blurring or smearing of the postmark. Both this property and the property of indelibility involve the question of the rate at which the ink penetrates or is absorbed by the fiber of the paper. A satisfactory ink does not harden or form a crust on the ink pad on exposure to the air. There must be no deposition of solid matter on the bottom of the vessel in which the ink is stored, and the pigments, on which the indelibility of the ink depends, if insoluble, must not settle out in such a way as to make it possible to pour off from the top of the container a portion of the ink which contains little or none of the insoluble pigment or pigments. The following methods have been found of value for the purpose of ascertaining the quality of a given sample of ink as well as the appropriateness of certain materials used for the manufacture of canceling inks

I.—METHODS FOR THE INVESTIGATION OF INKS MADE WITH AN OIL BASE.

1. Preparation and Care of the Sample.

Since canceling inks contain more or less insoluble and volatile matter, special attention must be given to the preparation and care of the sample. It must be carefully mixed by shaking before each portion is removed for analysis, and the container must be left open no more than is absolutely necessary for the removal of portions of the ink.

2. Determination of Matter Volatile at Ordinary Temperatures.

Place a carefully weighed quantity (between 5 and 5.2 grams) of the ink in a flat-bottomed aluminum dish 102 mm (4 inches) in diameter. Distribute the ink completely over the surface of the bottom of the dish by gently tilting the same. This quantity of ink should be sufficient to completely cover the bottom of the dish. Place the dish on a horizontal shelf or table where air will have free access to it and where it will be screened in such a way that no dust can fall into it.

Reweigh the dish at the end of 18 hours, 24 hours, 2 days, 3 days, 4 days, 5 days, 6 days, 7 days, 14 days, 21 days, and 28 days. Calculate the total percentage loss of weight at the end of each period of drying. The loss of weight should be gradual and should not exceed 15 per cent during the first 7 days, nor 25 per cent during 28 days. This test shows the absence of highly volatile ingredients and the absence of an excess of matter volatile at the ordinary room temperatures. The constituents of a canceling

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ink should be such that the volatile matter will not exceed the above limits when the ink is exposed under the conditions named to a summer temperature of 80° F. and upward.

3. Determination of Relative Penetrating Power.

(1) *Apparatus.*

(*a*) Homeopathic shell vials about 8 cm long and 2 to 2.5 cm in diameter.

(*b*) Strips of white blotting paper, which for a given series of determinations should be cut from the same sheet and of exactly the same dimensions. A convenient size is 12 mm wide and 25 cm long.

(*c*) A pair of dividers with arms 15 cm long or longer.

(*d*) A millimeter rule.

(2) *Determination.*

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

At the expiration of exactly 15 minutes from the time each strip is inserted in the vial, measure the height to which the liquid has ascended the strip of paper by means of a pair of dividers and record the distance in millimeters. A second set of readings may be taken at the end of 30 minutes or 45 minutes.

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

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

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

these solvents and the extent to which the lampblack has passed up the strip of blotting paper are indices of the quality of the ink.

An examination of the strips with the microscope will give valuable information regarding the rise of carbon in the paper and the affinity of the dye for the fibers of the paper. With many inks the carbon will not rise above the surface of the liquid, while with others it penetrates the paper to the same height as the dye. With this class of inks it is important that the base of the ink have the power to carry the carbon well into the fibers of the paper.

4. Sedimentation Test.

(1) *Apparatus.*

(*a*) Glass-stoppered cylinders, graduated for 200 cc and fractions thereof, the distance between the bottom and the 200 cc mark being 25 cm (10 inches). Failing these, other cylinders may be substituted, marks being placed at distances 25 cm (10 inches) and 16 mm ($\frac{10}{16}$ inches) from the bottom.

(*b*) A pair of dividers with arms 15 cm long or longer.

(*c*) A millimeter rule.

(*d*) Pipettes made from straight tubing (7 mm), at least 30 cm in length and having a capacity of from 10 to 15 cc.

(2) *Determination.*

By means of the special pipette introduce carefully, drop by drop, into one of the 200-cc cylinders, exactly 16 mm depth of the ink to be tested. To this add petroleum ether (boiling point 50°–60°), ordinary ether, alcohol, benzol, anilin, or other solvent which has been found by previous tests to be suitable for the base of the ink as well as for the dye, until the 200-cc mark is reached; stopper, and shake thoroughly. Allow the cylinder to stand, and record from time to time, by using the dividers and millimeter rule, the height of the top of the layer of sediment which collects in the bottom of the cylinder, expressing results in millimeters. During the first hour observations should be made at intervals of 15 minutes; later, each hour for several hours successively, and then twice daily for a week to ten days.

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

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

5. Determination of Lampblack.

Load a porcelain gooch with asbestos, using a felt about one-fourth of an inch thick. After washing the felt thoroughly with water to remove fine particles, finally wash with alcohol and ether, dry, and weigh. Weigh out about 5 grams of ink in a small beaker, dilute with a suitable solvent (alcohol is used in case of rosin-oil inks), transfer to a gooch crucible, and wash until all oil and soluble color is removed. Finally, wash with alcohol and ether, dry, and weigh.

6. Determination of Ash.

The lampblacks prepared for the manufacture of canceling ink yield less than 0.5 of 1 per cent of ash when burned, and the coal-tar dyes employed should contain no mineral matter other than that which is an essential part of the molecules of the substances to which the tinctorial power of these dyes is due.

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

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

7. Resistance of Pigments and Dyes to Light and Reagents.

It is necessary in the case of canceling inks, and important, if not necessary, in the case of many stamping inks, that the pigments and dyes employed in their manufacture be as resistant as possible to means which may be employed for the erasure of marks made by them on paper. Under this heading may be mentioned also the importance of the use of dyes which possess considerable affinity for vegetable fibers. It is not practicable to enumerate the agents which should be employed in experiments to ascertain the resistance of a given dye to erasure, as light, heat, and all of the solvents and reagents known to the chemist are available for the use of persons who might desire them for use in assisting them in making fraudulent erasures.

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

II.—METHODS FOR THE INVESTIGATION OF RUBBER-STAMP INKS.

1. Preparation and Care of Sample.

The precautions given in regard to the care of samples of inks made with an oil base should be observed.

2. Change of Weight on Exposure to Air.

This determination should be conducted in the manner described for the determination of volatile matter in inks made with an oil base. Rubber-stamp inks, however, gain or lose in weight according to the constituents used in their manufacture and according to atmospheric conditions. A rubber-stamp ink should not, however, undergo very much greater changes in weight when exposed to the air under given conditions than diluted glycerin containing 75 per cent of glycerin and 25 per cent of water by volume.

3. Penetrating Power.

This test should be conducted in the manner described above for inks made with an oil base.

4. Sedimentation Test.

This test should be conducted as described for inks made with an oil base, with the exception that the portions of ink should be diluted with water instead of petroleum ether.

5. Determination of Lampblack and Other Constituents.

A scheme of analysis similar to that described above for inks made with an oil base should be employed. Some experiments will be necessary in most cases to ascertain the proper solvent to be used in the case of each sample of ink to be examined. Alcohol, however, will generally be found to be satisfactory for rubber-stamp inks.

The amount of coloring matter contained in the alcoholic extract can be ascertained by spectro-colorimetric or by comparative dyeing tests. Both of these methods involve the previous identification of the dyes present by qualitative tests.

For the quantitative determination of glycerin in canceling inks the Hehner method[a] was found to be the most satisfactory. In using this method an excess of ferrous ammonium sulphate was added after the completion of the oxidation and this excess determined with standard bichromate solution. In this way a more satisfactory end point was obtained.

6. Resistance to Light and Reagents.

The remarks made above in regard to the investigation of the resistance of cancellations made with oil inks apply in general to canceling and other inks for use with rubber stamps.

III.—METHODS FOR THE INVESTIGATION OF MATERIALS USED FOR THE MANUFACTURE OF CANCELING AND OTHER STAMPING INKS.

1. Volatility and Penetrating Power.

The methods which have been described above will be found useful in determining the suitability of liquids for use as bases or constituents of bases of canceling and other stamping inks.

2. Sedimentation Test.

A modification of the sedimentation test described above may be employed with good results for the purpose of ascertaining the suitability of lampblack and other pigments for use in the manufacture of canceling and other stamping inks. The results, of course, are mainly of value for purposes of comparison.

The conditions of the test may be modified to suit the purposes of the investigation and the character of the materials to be compared. The writer has obtained good results in the comparison of lampblacks and other blacks rich in uncombined carbon by the following method, which was so planned that the results might be applied to stamping inks made with either a water-soluble base or an oil base:

Mix 0.5 gram of the black to be tested in a mortar with dilute glycerin (87.5 cc of glycerin diluted with water to 1 liter). Rinse the mixture into a 100 cc Nessler cylinder and dilute to the 100 cc mark, using the same dilute glycerin. After having prepared a series of tubes, each containing a portion of one of the blacks to be tested, close each tube with a cork and shake thoroughly each tube successively, performing the operation as quickly as possible in order that the time of settling may be approximately the same in the case of each sample. Allow the cylinders to stand at rest in a place free from jar, and record from time to time the height of the sediment formed by the deposition of the blacks. When submitted to this test, a black which is suitable for the manufacture of a canceling or stamping ink should occupy a volume of not less than 25 cc when the sediment has stopped settling.

3. Ash, etc.

Blacks, dyes, and other substances used for the manufacture of canceling and other stamping inks should be carefully examined to insure the absence of considerable percentages of substances which are not essential to the production of an ink of good quality. It can generally be assumed that the presence of considerable quantities of any substance which does not actually contribute to the desirable qualities of the ink will detract therefrom.

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[a] J. Soc. Chem. Ind., 1889, **8**: 4.

Black pigments rich in carbon of high specific gravity due to the presence of a large percentage of ash are highly unsuitable for the manufacture of stamping inks. Only the concentrated brands of coal-tar dyes should be used, unless the substances with which the less concentrated are diluted have been found to actually contribute to the working qualities of the ink to be produced.

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Revised by L. S. MUNSON, *Chief, Contracts Laboratory.*

Approved:

JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *May 1, 1905.*

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[a] Deceased. The original Circular No. 12 was prepared by Mr. Ewell when assistant chief of Bureau, being dated January 29, 1903.

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