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IRON GALLATE INKS—LIQUID AND POWDER

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ABSTRACT

A study was made of iron gallate ink that contained 3 grams of iron per liter. Both ferric and ferrous salts and various solid acids were used. Three ink formulas were devised, one for ferric and two for ferrous salts. These inks do not deposit sediment readily and they are a little less corrosive to steel pens than the Government standard writing ink. Two of the formulas can be used to prepare ink powders that will comply with the requirements of Federal Specification TT-I-563, Ink; Writing.

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I. INTRODUCTION

Writing ink purchased by the U. S. Government under the specification¹ for this material is most commonly obtained in liquid form ready for use. The specification also includes ink in the form of a concentrated liquid or a powder. Concentrated inks have been used to some extent because their compactness facilitates distribution from a central purchasing agency. Ink powders are preferred for the same reason, but prior to 1932 all the powders submitted for tests failed to comply fully with the requirements of the specification. Some powders produced ink that was not of the iron gallotannate type, while the ink made from those which were of the iron gallotannate type lacked sufficient stability.

Writing inks purchased under the specification have not always given satisfactory service. The U. S. Post Office Department has complained at various times about the excessive corrosion of steel pens caused by the ink used in their stations. As a result, a general study of writing inks was undertaken in an attempt to prepare one that would be less corrosive to steel pens than the standard ink,

¹ Federal Specification TT-I-563, Ink; Writing (see table 1 for formula).

and which could be prepared in the form of a powder and still comply with the requirements of the specification.

An iron gallotannate ink is considered permanent because it contains iron. If and when the black iron tannate or gallate decomposes, the iron remains and can be used to restore the writing. The standard writing ink contains 3 g of iron per liter, and in order to have all the experimental inks on the same basis, this figure was used throughout the work. With this concentration of iron as a starting point, the other ingredients necessary to make an ink were studied by varying their concentrations or by substituting different types of materials. The characteristics of the experimental inks were determined by using the tests described in the specification. An attempt was made to evaluate the stability in terms of the number of days required for sediment to appear. The results obtained for any one ink were not strictly reproducible, but in testing a series of inks simultaneously, the results always placed the inks in the same order of stability. Finally three inks were prepared which were less corrosive to steel pens and more stable than the standard writing ink.

II. EFFECT OF ALTERING COMPOSITION WITH RESPECT TO CERTAIN INGREDIENTS

1. PHENOLIC BODY

The formula for the U. S. Government standard writing ink was derived from the formula for the standard record ink by halving the quantities of all the materials except the dye and phenol. The formula for standard record ink is almost identical with the one recommended by O. Schluttig and G. S. Neumann,² who made a very careful study of the subject.

Schluttig and Neumann showed that ink made with gallic acid produces writing that darkens more than that produced by ink made with other phenolic materials that give colored compounds with ferric salts. Since the amount of gallic acid they needed to prepare a liter of ink was larger than the amount of this substance that would dissolve in a liter of water, tannic acid was added to make up the difference. In their final ink, Schluttig and Neumann used 23.4 g of tannic acid and 7.7 g of gallic acid, with 30 g of ferrous sulphate, in 1 liter of ink. This ink contained 1.05 gram-moles of phenolic compounds for every gram-atom of iron.

Silbermann and Ozorovitz³ made a study of iron gallates and prepared a compound requiring 1 gram-mole of gallic acid for every gram-atom of iron. Their object apparently was to study the iron gallate compounds in the ink before it was put on paper.

Some time later F. Zetsche⁴ and his collaborators made a study of written characters. Their approach involved an oxidation reaction taking place in a dilute solution. The ink compound which they prepared from gallic acid was formed from 1 gram-mole of gallic acid and 1 gram-atom of iron. In order to check this point for the present work, two preparations were made. In the first, equimolecular quantities of ferric chloride and gallic acid were dissolved separately in alcohol and these solutions were mixed. In the second, 2 moles of

² Die Eisengallustinten, v. Zahn & Jaensch, Dresden (1890).

³ Bucarest. Bul. soc. stiinte 17, 43-57 (1908); Chem. Zentr. 1908 II, 1024.

⁴ Ann. Chem. 435, 233 (1924).

ferric chloride and 1 mole of gallic acid were used. Both precipitates contained approximately the same proportion of iron, which corresponded to the theoretical amount of iron in ferrigallic acid.

Inks have been made which contain a higher concentration of gallic acid than could be possible if the solubility of this material in water were the controlling factor. The U. S. Government formerly bought "Treasury Standard" copying ink that was based on a formula requiring 15.4 g of gallic acid per liter.⁵ An experimental ink showed that as much as 18 g of gallic acid can be dissolved in a liter of water containing 15 g of ferrous sulphate. Only 10 g of gallic acid is necessary if the ink is to contain 3 g of iron per liter.

It is well known that gallic acid inks have better keeping qualities than inks made with tannic acid, and since a sufficient quantity of gallic acid can be dissolved in a solution containing ferrous sulphate equivalent to 3 g of iron per liter, to make an ink, it is logical to eliminate the tannic acid. Inks prepared with decreasing amounts of tannic acid accompanied by increasing amounts of gallic acid were tested for stability, and the results are given in table 1. Those inks which contained gallic acid without tannic acid had the best keeping qualities.

TABLE 1.—Effect of gallic and tannic acid on stability of ink

Ink no.	Composition of ink in grams per liter of water						Stability in approximate days for sediment to form
	Tannic acid	Gallic acid	Ferrous sulphate, FeSO ₄ ·7H ₂ O	Ferric sulphate, anhydrous	Oxalic acid	Tartaric acid	
1 ^a	11.7	3.8	15	-----	-----	2.6	5
2.....	8.4	7.7	15	-----	-----	2.6	5
3.....	-----	10	15	-----	-----	2.6	10
4.....	11.7	3.8	-----	10.7	2.16	-----	7
5.....	8.4	7.7	-----	10.7	2.16	-----	35
6.....	-----	10	-----	10.7	2.16	-----	↳+42

^a Standard ink is similar to this formula, excepting that 12.5 g of dilute U. S. P. hydrochloric acid is substituted for tartaric acid, and 3.5 g of dye and 1 g of phenol are added.

^b +=test was stopped before sediment appeared.

F. F. Rupert⁶ found that inks containing gallic acid without tannic acid had a very low permanence when exposed to the weather. In the present work the relative permanence of the standard ink, which is essentially a tannic acid ink, and of inks containing only gallic acid was tested by exposing stripes in a Fade-Ometer for 150 hours. Both types of ink seemed to have the same degree of permanence.

2. IRON SALT

Ferrous sulphate is probably the only ferrous salt used in the preparation of ink. The pure heptahydrate is not hygroscopic, and it does not oxidize readily in air. These properties indicate the possibility of using this material for the preparation of ink powders. The ferrous sulphate used in this work was freed from ferric compounds by precipitation with alcohol.⁷

⁵ Cir. BS C400, 7 (1933).

⁶ Ind. Eng. Chem. 15, 489 (1923).

⁷ E. Thorpe, Dictionary of Applied Chemistry 3, 681. (Longmans, Green & Co., London, 1922).

Ferric salts have also been used in inks. The effect of substituting an equivalent amount of ferric sulphate for ferrous sulphate is shown by comparing the corrosiveness of inks 9 and 10 in table 2. Since it is known that the dye has no corrosive effect, the increase in corrosiveness is due to the use of ferric sulphate. Apparently it is immaterial which ferric salt is used. Inks prepared respectively with ferric chloride, ferric chlorosulphate, or ferric sulphate showed no marked differences in keeping qualities or corrosion of steel pens. B. Walther⁸ published several formulas for inks containing ferric chlorosulphate hexahydrate, a patented salt which is not hygroscopic. This salt was most successfully prepared by oxidizing an aqueous solution of ferrous sulphate with chlorine gas. The product contained less water than the hexahydrate, but in other respects the analysis checked with the theoretical formula.

Ferric sulphate was used to prepare the ferric inks because this material is not as hygroscopic as ferric chloride and it can be obtained more readily than ferric chlorosulphate. Since the ordinary reagent grade of ferric sulphate is not anhydrous, the material was analyzed for iron, and a sufficient quantity to give the desired amount of iron was used.

In the preparation of ink powders, materials that do not take up sufficient water to cause the prepared powder to form a cake are desired. In order to determine the behavior of those iron salts which seemed likely to fulfill this requirement, three powders were prepared, using ferrous sulphate crystals in the first, ferric sulphate in the second, and ferric chlorosulphate in the third. These powders were put in open test tubes and kept in an atmosphere of 50 percent relative humidity. The powder containing ferric chlorosulphate began to form a cake after 1 month, whereas the other two were still loose after 2 months. With moderate protection from atmospheric moisture, either ferrous sulphate crystals or anhydrous ferric sulphate is suitable for making ink powders.

3. STABILIZING AGENT

Inks contain acids to improve their keeping qualities. In general the acid prevents the formation of the basic iron salt, which is more readily oxidized than the normal compound. J. W. McBain⁹ points out that sulphuric acid tends to improve the stability of ferrous sulphate solutions, whereas hydrochloric acid has the opposite effect on solutions of ferrous chloride. No information was given on the behavior of ferrous sulphate solutions containing hydrochloric acid, but it seems reasonable to believe that the behavior of this combination ought to be similar to that of the ferrous chloride solution containing hydrochloric acid. In an ink, the difference in the effect of hydrochloric and sulphuric acids is not noticeable, and for all practical purposes they may be interchanged, but from the above information it seems advisable to use sulphuric acid instead of hydrochloric acid. Tartaric, citric, and succinic acids were also used as stabilizing agents, and the resulting inks had practically the same keeping qualities as the standard ink. Of these three, tartaric acid was preferred because it is cheaper than the others. Oxalic acid cannot be used in inks containing ferrous salts because it precipitates

⁸ Chem.-Ztg. 45, 842 (1921).

⁹ J. Phys. Chem. 5, 623 (1901).

the iron as ferrous oxalate. This acid can, however, be used with ferric salts. Walther's formulas for inks containing ferric chloro-sulphate require oxalic acid.

The amount of acid used in the standard writing ink was originally the result of a compromise between stability and corrosion of steel pens. Since the keeping quality of an ink is increased by replacing the tannic acid with gallic, the amount of stabilizing acid can be decreased, and the resulting ink will be less corrosive to steel pens. The amount of hydrochloric acid in the standard ink is chemically equivalent to 2.58 g of tartaric acid or 2.16 g of crystallized oxalic acid. Since solid materials are necessary in the preparation of ink powders, these two acids were used as stabilizing agents instead of hydrochloric acid or sulphuric acid. The amount of tartaric acid necessary to stabilize a ferrous ink that contains only gallic acid is shown in table 2 by comparing the results of tests made on inks 7, 8, and 9. Only a little over one-third as much acid as the standard ink contains is necessary, and the resulting ink is less corrosive to steel pens.

TABLE 2.—Effect of acid content on corrosion and stability

Ink no.	Composition in grams per liter of water						Corrosion of steel pens in mg dissolved	Stability in approximate days for sediment to form
	Gallic acid	Ferrous sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Ferric sulphate anhydrous	Oxalic acid	Tartaric acid	Dye		
7.....	10	15	-----	-----	2	3.5	35	a 60+
8.....	10	15	-----	-----	1	3.5	24	60+
9.....	10	15	-----	-----	0	3.5	20	7
10.....	10	-----	10.7	0	-----	-----	62	4
11.....	10	-----	10.7	1	-----	-----	46	18
12.....	10	-----	10.7	1.5	-----	-----	28	18
13.....	10	-----	10.7	2	-----	-----	23	21
14.....	10	-----	10.7	2.5	-----	-----	16	25
15.....	10	-----	10.7	3	-----	-----	10	42+

a +=tests were stopped before sediment appeared.

Oxalic acid is used as a stabilizing agent in inks made with ferric salts because in addition to preventing the formation of sediment, this acid retards the corrosion of steel pens by forming a protective coating of ferrous oxalate on them. Other acids, such as tartaric, hydrochloric, or sulphuric, will not do this. The results of the corrosion tests for inks 11 to 15, inclusive, show the effect of varying the concentration of oxalic acid. The corrosion of steel pens decreases with increasing concentration of oxalic acid.

The results given in a previous publication¹⁰ show that inks made with oxalic acid have a marked deleterious effect on the aging of paper. Therefore, this type of ink is unfit for use in making permanent records.

4. PRESERVATIVE AND DYE

No experimental work was done on the use of a preservative to prevent mold growth on ink. Preservatives were not used in the experimental inks, and although the corks in the bottles became moldy, the inks were not affected.

¹⁰ J. Research NBS 14, 463 (1935) RP779.

No attempt was made to change the dye ordinarily used in preparing the standard ink. It was noted, however, that this dye seemed to retain its brilliance when used in inks that did not contain chlorides. In the standard ink, the color is likely to fade toward a greenish shade. Perhaps this is the color change found by Walther when he prepared inks containing ferric chloride.

III. CONCLUSION

Formulas for ink, either liquid or powder, can be readily worked out from the data given here. Three such formulas are given in table 3.

TABLE 3.

Ingredient	Ink		
	16	17	18
Gallic acid.....	10.0 g.....	10.0 g.....	10.0 g.
Ferric sulphate, anhydrous.....	10.7 g.....		
Ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$		15.0 g.....	15.0 g.
Oxalic acid.....	2.0 g.....		
Tartaric acid.....		1.0 g.....	
Sulphuric acid ^a			0.654 g.
Soluble blue (C. I. 707).....	3.5 g.....	3.5 g.....	3.5 g.
Water to make.....	1 liter.....	1 liter.....	1 liter.

^a Calculated as anhydrous H_2SO_4 .

Inks 16 and 17 can be prepared as powders which, when dissolved in the proper amount of water, will produce ink that will comply with the requirements of Federal Specification TT-I-563, Ink; Writing. Ink 18 embodies the same characteristics as ink 17, except that it cannot be prepared in powdered form. To make a gallon of ink, the figures in the table must be multiplied by 3.79. These three inks are more stable and less corrosive to steel pens than the standard ink. Of these three inks, ink 16 is inferior to inks 17 and 18 because it has a lower stability and it contains oxalic acid, which attacks paper readily and tends to form a crust on steel pens. The stability of inks 17 and 18 makes them particularly suitable for use in fountain pens.

WASHINGTON, May 10, 1935.