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Black Writing Ink of the Colonial Period

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THERE are many conceptions concerning the composition of seventeenth and eighteenth century black writing inks. The most prevalent include the beliefs that they were made from berry juices, rusty nails, soot, or other substances which would produce a color in an aqueous solution. The ink formulae compiled in Table I were found in local Virginia manuscripts as well as American, English, and Continental publications which are known to have been in use during the period of this study. They substantially discredit these widely held misconceptions as does an examination of experiments in inkmaking as reported by researchers of that age. Tests on a large number of early documents, with particular regard to the effects on the permanency of the manuscript by the inks with which they were written, indicate that iron gall inks were used almost exclusively. It was found that inks of this type were in use even several centuries before the period of this study.

Petrus Maria Caneparius, a Venetian physician, was the most outstanding ink scientist of the seventeenth century. He devoted to inks a large part of his *De Atramentis* which was first published in 1619 and reprinted in 1660. His descriptions of inkmaking are often quaint, a chemical reaction reported in lengthy detail being frequently characterized as "a marvel of nature." A century later, Dr. William Lewis of England, in his *Commercium Philosophico-Technicum,* printed in 1763, outlined principles of inkmaking which are being used today. As a result of his experiments, definite improvements were made in iron gall ink formulae. *The Dictionary of Chemistry and Mineralogy*, 1807, by Arthur and Charles R. Aikin, supplies a great deal of historical information regarding the sources and preparation of the ingredients of ink. These books have been used extensively in this study. Among the modern works consulted were those of Dr. C. E. Waters, formerly chief of the Section of Organic Chemistry, National Bureau of Standards, Dr. C. A. Mitchell of England, and Elmer W. Zimmerman, Charles G.

Weber, and Arthur E. Kimberly of the Paper Section, National Bureau of Standards. These and other sources are cited in the bibliography at the close of this paper.

Among the formulae found in the early publications were a number for making India or Chinese ink. These inks were composed basically of carbon, and were never recommended as a writing fluid. As a rule, these carbon inks were a paste, applied to paper with a brush as they are even today in the Orient. As the quill pen was the common writing instrument used in both America and England, a fluid writing ink was a necessity. In one instance lamp black was suggested for a portable ink and in another as a means of restoring blackness to deteriorated iron gall ink that had turned brown in an inkwell. The unpopularity of carbon inks in a liquid state was due to the failure of the black particles to stay in suspension, the tendency of the ink to smudge in damp weather, and the fact that they could be washed from the document. These inks were composed primarily of water, a gum, and lamp black or ivory black. The latter two pigments contained various oils which added to the difficulty of getting the black particles in suspension. Although this type of ink was most resistant to fading and seldom contained compounds injurious to paper, it was seldom used. No formula for black ink was found which did not contain carbon, or iron and galls.

If compounded with the proper amount of gum arabic, the iron gall inks flow easily from a quill pen, penetrating the fibers of the paper to form a black insoluble compound. Writing in these inks is quite difficult to bleach or remove from paper without leaving some evidence of alteration, qualities highly valued in an ink and often mentioned in the formulae as being the principal reason for their use. The basic ingredients were copperas, galls, gum arabic and a solvent such as water, wine, vinegar, ale or beer. If these materials were blended in the proper proportions, the ink would have a high, black luster, greatly admired by some inkmakers.

Examination of documents of this period reveals that the iron gall inks have either remained black, turned rusty brown, or faded out completely. The latter will be found to have occurred only in a small fraction of one percent if several thousand documents are inspected. During the middle of the eighteenth century, Lewis made the first investigation to determine the principal cause of this turning of black iron gall ink to brown. After exposing inks of different composition to several weeks of sunlight, a procedure still used today, as well as performing other tests, he came to the conclusion that the insufficient use of galls was the primary cause. He recommended that compounding three parts, by weight, of galls to one of copperas would make the most durable ink. Later analyses of galls and the method used at that time for extracting the tannic and gallic acids they contained have shown that his recommendations in the main were correct. Few inks made from the formulae in Table I could be expected to remain black over a period of years. Recent research has shown that the composition of paper as well as storage conditions can be factors in turning black iron ink brown.

Another very interesting observation by Lewis was what he termed the corrosive effect of these iron inks on documents of an earlier period. He concluded this was due to acid in the ink and unsuccessfully attempted to neutralize it with lime. Kimberly, Zimmerman and Weber in their study of gallotannate of iron inks in 1935 also concluded the mineral acid in these inks to be destructive to paper. In the process of inkmaking, sulfuric acid is produced when the gallic and tannic acids of the galls combine with the iron in the copperas (ferrous sulfate) to form the black writing fluid. This acid does not evaporate when the ink dries but spreads into the fibers surrounding the inked area, causing eventual embrittlement of the paper. It will be shown later that the presence of high acidity in these inks has caused deterioration in a large number of colonial documents. Inks having a relatively low acidity have done but slight damage.

A study of the materials that produce these inks is interesting as well as helpful in evaluating the effects that they have had on the permanency of documents. There were two most important compounds, copperas, sometimes called green vitriol, sal martis or sulfate of iron, today technically known as ferrous sulfate, and galls. Copperas was made by the oxidation of pyrites on exposure to air and, according to Aikin, the process had, by 1807, changed but little since the reign of Queen Elizabeth. Rain water was allowed to dissolve and carry off into a lead chamber the copperas and sulfuric acid, formed by the oxidation of the mined pyrites. Scrap iron was added to this solution which was heated for six days. A greater yield of copperas was obtained by this addition due to the interaction of the iron and sulfuric acid. Aikin further states that the same process was followed in France, but that in Germany no scrap iron was used. A description of the process can be found in *Philosophical Transactions*, Vol. XII, 1678. In view of the lack of analytical methods employed at that time for testing acidity, one can readily see how one quantity of copperas would vary from another in residual sulfuric acid. This would inevitably result in some inks being more acid than others. The clear green crystals of copperas were often recommended for inkmaking in preference to those containing ochre (basic ferric sulfate.) The purest copperas then available and used primarily in medicine was produced by dissolving iron in sulfuric acid. With one exception, copperas was the only source for obtaining iron to combine with the gallic and tannic acids. This exception was the solution derived from nails soaked in water for ten or twelve months. It is very doubtful that this procedure was ever used when copperas was an almost necessary ingredient for the then prevalent practice of dyeing cloth in most households.

Galls, the second most important ink ingredient, contain tannic and gallic acids which combine with the iron in the copperas to form a black pigment. The gall is an excrescence produced when the commonly called gall wasp punctures the bark of an oak tree and deposits an egg. When the larva develops, the tree produces the gall which serves not only as a home but as food for this insect. If the larva dies or leaves at a certain stage, the tree discontinues the production of tannic and gallic acids within the gall. This gall is of greatest value to the inkmaker when it contains the maximum amounts of those two acids. The blue or Aleppo gall was recognized and recommended in most ink formulae as being best for the purpose. According to Aikin, they were about the size of a nutmeg and were imported from Syria or other parts of Asia Minor. The brown English galls "vulgarly called oak-apples," and those produced in southern Europe were inferior to the Aleppo in tannic and gallic acid content. Aikin further states that Davy extracted 12.5% soluble matter from ordinary galls, and 46% from Aleppo, the latter extract containing about 90% gallic and tannic acids. Modern methods of extraction have increased this yield considerably. Recent work by Mitchell has shown that the Aleppo gall had from 52.9% to 79.5% tannic and 2.5% to 11.2% gallic acids, while the British gall contained only 3.2% to 36.7% tannic and 0.0% to 1.5% gallic acids. As a rule, the ink formulae recommended from four to twelve days, in the sun in summer or by the fire in winter, to properly extract the "virtue of the galls." Fermentation as well as heat were both factors in this extraction process. The common practice of breaking the galls into pieces before soaking was discontinued by Lewis as he found through experimentation that, by reducing them to a powder, he obtained a greater yield of these two organic acids. Boiling the galls for different lengths of time was advocated in several formulae. Caneparius recommended boiling the mixture as long as it takes to say "three pater nosters." These two organic acids were generally referred to as "astringents" a term still used in medicine. Lewis as well as others realized that oak bark, sloe bark, sumach, and pomegranate peels contained these acids, but he could not extract them in sufficient concentration for inkmaking. Both gallic and tannic acids are extremely weak and according to the findings of Kimberly, Zimmerman and Weber in 1935 they are not injurious to paper. This is the general concensus of opinion of other ink chemists.

Aikin says that gum arabic came primarily from Egypt and the Levant, that it "oozes" from a specie of the mimosa tree and hardens into round, yellowish white drops about the size of partridge eggs. Aikin may have been misinformed, the acacia tree and not the mimosa being the chief source of gum arabic. It is usually referred to as gum, and once Caneparius, who called it the "tears of Arabia," states that it gives body to the ink and keeps it from flowing too easily. Lewis attributes the following properties to the gum: it gives viscosity or body to make ink flow well, prevents the ink from spreading, suspends coloring matter, and does not sour easily. The writer has found that the gum is necessary to make ink flow properly when writing with a quill pen. This is not true when using a modern steel or fountain pen. The above evidence indicates that its purpose was to give the proper viscosity to the liquid and not to glue the ink particles to the paper as some modern chemists have assumed. Recent investigation has not shown that gum arabic is injurious to paper.

Rain water was the solvent most often recommended in inkmaking, being the purest water generally available at that time. Spring and river water were specified in a few cases. In some areas, these waters are so alkaline that the content of the mineral acid in ink made with them would be slightly reduced due in most instances to presence of bicarbonate of calcium. The second most frequently recommended solvent was white wine. Lewis states that white wine gave a better color to ink when first made and that this effect was more pronounced with vinegar. Some of the other points of interest with respect to wine as a solvent are the possibly increased solubility of the gallic acid of the galls due to the alcoholic content, and the slightly inhibiting effect on mould and bacteria. However these factors would be eliminated by the evaporation of the alcohol unless the container remained closed at all times. The pleasant, ethereal odor given off by the wine no doubt appealed to the makers and users of ink, and it may have been another one of the reasons for its use. As a rule, wine is slightly acid and will later be shown to be detrimental to paper. Vinegar, which was occasionally used, also proved to be somewhat injurious to paper.

Aqua vitae, brandy or spirits were sometimes added to keep the ink from freezing and breaking its container. This was no doubt a problem in cold climates where only limited heating facilities prevailed. However, it is interesting to note that Waters in his tests at the National Bureau of Standards did not encounter this difficulty when he froze ink in a refrigerator. The capital imperfections created by the addition of distilled spirits seem to have been the decreased solubility of the copperas, the tendency of the ink to feather on paper, and the fact that its black color faded more quickly when kept in an inkwell. Some of the eighteenth century inkmakers condemned this practice for these reasons. Among other ingredients sometimes added were rock alum, pomegranate peel, feces, sugar, bark of the nut tree, and copper sulfate. No reason was given for the use of rock alum which was described by Murray as alunite or alum stone from Italy. The peel of the pomegranate and the nut tree bark contained tannic acid which accounted for their use. Sugar would give a gloss to the ink, an admired characteristic, as well as prevent it from drying quickly. This quality assisted in making letter press copies toward the middle of the eighteenth century. Copper sulfate was believed to add blackness to the ink. These ingredients, with the occasional exception of rock alum, are rarely mentioned in the investigated formulae.

When first made, iron gall ink has but little color, freshly written characters being difficult to read. The tannic and gallic acids of the galls combine with the ferrous iron of the copperas to form a soluble and invisible compound, which remains so until the oxygen of the air converts it to the ferric state. This latter compound which is black and insoluble is known today as gallotannate of iron. The early inkmakers took advantage of this point and allowed some of the ink to become oxidized in order that it would have sufficient blackness to be used as a writing fluid. When wine or vinegar is used as a solvent, the ink becomes darker more quickly than when distilled water is used. This was the principal reason for their use. Toward the middle of the eigtheenth century logwood extract was often used to give this added color. In 1763, Lewis experimented with the juices of various berries, but found they had a detrimental effect on the color when exposed to sunlight. He recommended logwood which has since been replaced by other organic dyes.

There were various procedures used in compounding iron gall inks, but the following as recommended by William Allason of Falmouth, Virginia, in his *Letter Book*, 1770-1787, Archives Division, Virginia State Library, is typical of these two centuries:

Arabic, three ounces; vitrol (green vitrol) two ounces Galls, three ounces; white wine two pints and a half; beat the Galls put them with the wine into an earthen vessel, set it in the sun for six days, stir them every day twice or thrice, then sit it over a moderate fire for a half a day or a day; then strain it having dissolved some vitrol and Gum in a little wine, put it into it, then set it in the sun three days more, and it is made. To keep it from freezing put into it a little aqua vitae — You may use Rain or River water instead of wine.

If the often quoted Caneparius had written the above, he would have likely added, "We thus have Encaustum, Indeed, Indeed, a marvel of nature." It is not known whether William Allason used ink made by this formula when writing his letter book. If he did, the lack of sufficient galls would be one of the principal reasons why the ink has turned brown.

Another ink which was in demand to some extent was a kind of powder which was often called a portable ink, being suitable for carrying on a journey. In the seventeenth century this was usually made by reducing the galls, copperas, and gum arabic to the finest possible state, sifting the powder through a cloth, and adding water or wine to the powder as needed. Caneparius called this ink-dust and stated that this was not used as extensively as the regular liquid ink. It was quite pale when first made, limiting its use. In 1764, directions for making an ink powder were printed in *The Handmaid to the Arts* and consisted of evaporating the liquid ink in a balneo mariae (water bath) and powdering the residue. It would write as black when water was added as it did before evaporation. It is not known when this type of ink was first used. Evidence has been found of ink powder that had fallen in the inner margin of record books as early as 1680. It was often advertised for sale in the *Williamsburg Gazette* during the eighteenth century. One can readily see the advantage of purchasing a powder that would serve its purpose well, avoiding the necessity of going through the procedure for making ink already described. Goyer of Paris is credited with establishing the ink industry in 1625, but whether he manufactured a powder or liquid ink has not been determined. The former type would surely have been easier to package, ship, and protect from freezing or spoilage by mould and bacteria. For these various reasons, it would seem that this ink powder may have been much used in this country during the eighteenth century.

Various containers were suggested for storing ink until used.

Caneparius's recommendations were unique and were as follows: "Keep the ink in a lead vase, for lead increases the blackness. The ink can be kept, however, in a glass vase, if the vase is thoroughly cleaned. You can also keep it in a vitreous potter's vase, or in a gourd which has hardened with age. Container should be kept closed or at least covered, so as to keep out the dust which will mess up the ink in a marvelous manner." Lewis suggested an oaken cask as the astringent material in the wood is the same as that found in galls. He warned against the use of copper or lead containers which he stated would "debase the color of ink." He further recommended placing small pieces of iron in the cask to reduce the acidity of the ink. The ferrous sulfate thus formed would make the ink less acid. To what extent this was practiced is not known, but in the literature studied Lewis makes the only suggestion for eliminating this acidity. The containers used for packaging ink powders could be of a much simpler nature and were likely made of paper. A communication dated 19 Dec. 1782 from L[eighton] Wood to James Simmons requesting "half dozen papers of Ink Powder" seems to substantiate this idea. This document may be found in the Executive Papers in the Archives Division of the Virginia State Library.

TABLE I

IRON GALL INK FORMULAE OF THE SEVENTEETH AND EIGHTEENTH CENTURIES EXPRESSED IN GRAMS PER 100 C.C. OF SOLVENT

No.	Date	Copperas	Galls	Gum Arabic	Rock Alum	Logwood	Solvent	Bibliography
1	C. 1600	3.1	6.2	12.4			Spring water	14
2	" "	9.3	12.4	12.4	12.4		Rain water	"
3	" "	3.1	6.2	12.4			Ale	"
4	1602	9.3	15.5	6.2			Wine or rain water	5
5	1619	3.3	9.9	6.6			White wine	4
6	"	6.6	9.9	6.6			" "	"
7	"	2.5	10.0	5.0			" "	"
8	"	19.8	13.2	6.6			" "	"
9	"	2.5	10.0	5.0			" "	"
10	"	6.0	4.0	4.0			White wine or vinegar	"
11	"	10.0	15.0	10.0			" " " "	"
12	"	12.5	6.2	6.2			Wine from Mallows	"
13	1656-66	2.3	3.1	1.5			Rain water	16
14	1727	1.5	9.3	6.2	3.1		" "	5
15	1735	6.0	12.0	6.0	6.0		" "	7
16	"	3.5	5.6	some			" "	"
17	"	6.3	6.3	2.1			" "	"
18	"	4.2	6.3	some			" "	"
19	"	6.0	12.0	6.0		24.0	White wine	"
20	"	3.0	12.0	6.0			Rain water	"
21	1751-65	24.8	49.6	6.2			" "	8

22	" "	8.0	6.0	2.0	3.0		River water and white wine	"
23	1753	6.2	12.4	6.2			Rain water	9
24	1760	6.2	12.4	1.5	1.5		Soft water	6
25	1763	3.1	9.3	some		3.1	Vinegar or white wine	12
26	1764	6.2	12.4	3.9	1.5		Soft water	10
27	"	6.2	12.4	2.7		12.4	" "	"
28	"	8.0	00.0	2.0			" "	"
29	"	3.7	7.4	2.3			" "	"
30	1770	3.1	12.4	3.1			Rain water	14
31	"	6.2	24.8	4.7	1.5		Equal parts rain water and vinegar	"
32	1770-87	5.0	7.5	7.5			White wine or river water	2
33	1777	9.1	7.5	6.0			Beer	18
34	1792	4.1	8.2	4.1		4.1	Water	14

These additional ingredients were recommended in the indicated formulae: No. 5, 9.9 g. pomegranate rind; No. 6, handful of ash bark; No. 8, handful of nut tree branches; No. 14, sugar loaf size of a hoarsel nut; No. 19, 6.0 g. pomegranate peel; No. 20, feces; No. 27, privet berries may be substituted for logwood, 1.5 g. pomegranate peel; No. 28, 8.0 g. pomegranate peel; No. 29, evaporate to dryness to make ink powder; No. 31, 0.75 g. verdigris; No. 33, salammoniac to prevent moulding; No. 34, 1.0 g. copper sulfate.

A survey of seventeenth and eighteenth century documents was made to determine which type of iron gall ink appeared to have had the most detrimental effects on paper. After examining several hundred specimens, fifty were found in which the ink had eaten holes through the paper. Of the fifty, the ink of three was brown, that of forty-seven was black, a strong indication that the latter was more destructive. Most of these holes occurred in capital letters or other places in which there was a large deposit of ink. High acidity in these inks and its destructive effect on paper have been known for a long time. As early as 1763, Lewis considered this to be the chief cause for the damaging effect of iron gall inks on paper. He, as well as others, tried to produce a permanent iron ink free of acidity yet retaining all of the desirable properties of a good writing fluid. Not until very recently did the work of the Section of Organic Chemistry of the National Bureau of Standards and the laboratory of the Government Printing Office make this possible in an ink first discovered in 1908 by Silberman and Ozorovitz of Rumania. This new ink is composed of iron, ammonia and gallic acid, and is technically known as diammonium hydroxyferrigallate. Details on a manufacturing procedure for this ink as developed by Morris S. Kantrowitz and Earl J. Gosnell may be found in *Alkaline Writing Ink*, Technical Bulletin No. 25, 1947, of the United States Government Printing Office.

A test for acidity on the inked and uninked areas of several old documents of the period seemed desirable. This test was limited to fourteen sheets that were considered of no historical value and were either purchased or given to the writer for this purpose. The pH of these papers was determined colorimetrically and the method of preparation of the sample was the same as that developed by Dr. Herbert F. Launer of the National Bureau of Standards. The results of these tests may be found in Table II which clearly indicates that the black inks were far more acid than the brown. In all cases, except one, the inked area was more acid than the uninked margins. A pronounced discoloration and embrittlement was noticed in the inked portion of samples 1, 2, and 3. In samples 2 and 3 holes appeared in the heavy or broad pen strokes. Since these specimens seem to be a fair cross section of the documents of this period, it is only logical to assume that iron gall inks varied from a low to a very high acid content. It is interesting to note that the paper in the inked areas of specimens 1, 2, and 3 of Table II could be reduced to powder when pressed between the fingers. The uninked margins could be handled without fear of injury. These three documents were excellent examples of the ultimate effects of highly acid ink on paper.

TABLE II

pH of Inked and Uninked Areas of Documents

No.	Approx. date	Appearance of paper	No. sides written on	pH uninked margin	pH inked area
		BLACK WRITING			
1	1669	very brittle	2	4.4	3.7
2	1715	" "	2	4.3	3.4
3	1740	" "	2	4.2	3.5
4	1712	weak	1	4.8	4.0
5	1690	good	2	6.4	5.4
		BROWN WRITING			
6	1770	weak	1	4.9	4.7
7	1744	good	1	5.1	5.1
8	1745	fair	1	5.0	4.8
9	1799	fair	2	4.4	4.2
10	1784	good	1	4.8	4.7
11	1747	weak	2	4.7	4.4
12	1744	fair	1	5.0	4.8
13	1710	brittle	2	5.1	4.1
14	1745	fair	1	5.0	4.8

There are two distinct types of inks found in Table II. As stated, the first has remained black for several hundred years while the second has turned a rusty brown. The proportion of galls to the amount of copperas used varied considerably in the formulae given in Table I. The brown writing, which was originally black, lost its color due to insufficient amounts of gallic and tannic acids in the inks. The inks which have remained black contained sufficient tannic and gallic acids to balance the quantity of iron in the copperas. As too few galls were included in most of the formulae, the ink in the majority of old documents has turned brown. This principle was first discovered by Lewis, and the work of later researchers has confirmed his findings.

It seemed desirable to reproduce as nearly as possible these two types of inks in order to best study their effects on the permanency of paper. After analyzing the formulae in Table I, two inks, considered to be of average composition, were made. Ink A6 contained 6.0 g. ferrous sulfate, 3.0 g. gum arabic, 4.68 g. tannic acid, 1.52 g. gallic acid, and 100 c.c. distilled water. These proportions are similar to the formula recommended by Waters as a permanent black ink with the exception of the addition of gum arabic. Ink B6 was the same in every respect with the exception that the amounts of tannic and gallic acids were decreased to one-fourth the amounts used in A6. Within a short course of time, ink B6 can be expected to turn brown. Ink lines were drawn with a quill pen on both sides of two eighteenth century papers. These lines were in width of one inked line to four uninked spaces. This was estimated to be about the proportions resulting when a scribe wrote with a wide point quill and formed his letters fairly close together. These specimens were heated for 72 hours at 100° C. which is the procedure used for evaluating the stability of papers by the National Bureau of Standards and other laboratories. The folding endurance test was used to determine the embrittlement of the paper fibers that might result from the ink. The pH (degree of acidity) of the inked and uninked specimens were also made. Data on these experimental inks is given in Table III.

TABLE III

INK A6

% Retention	Date of Paper	1 Uninked	2 Inked	3 Inked Solid	4 Ink Powder	5 Neutralized
Folding	1722	96	55	00	64	107
Endurance	1790	88	58	00	75	117
pH after	1722	7.6	6.9	3.1	7.5	7.7
aging	1790	5.7	4.8	3.2	5.1	7.3

INK B6

% Retention						
Folding	1722	96	74	11	79	91
Endurance	1790	88	61	9	80	103
pH after	1722	7.6	7.4	3.5	7.6	7.9
aging	1790	5.7	5.2	3.6	5.1	7.5

The uninked specimens showed but little decrease in folding strength under a cycle of artificial aging, while the inked papers exhibited a marked decrease. The acidity of the inked papers was higher than that of the uninked. The papers containing ink A6 decreased more in the fold test and had a higher acid content than did those containing ink B6. This factor was also exhibited in the survey as well as in the old papers of Table II. This difference in acidity may be accounted for by the formation of less free mineral acid in ink B6 when the gallic and tannic acids combined with the iron in the copperas, for ink B6 contained only one-fourth as much of these organic acids as did A6. Ink A6 was lower in acidity than the very acid black inks of Table II. However, if the concentration of the ingredients had been three or four times greater, which does occur in some of the formulae of Table I, then the acidity would have been more nearly equal. Evaporation of the solvent in the ink-well, closeness of the writing, surface of the paper, viscosity of the ink, width of the pen strokes, and residual acid in the copperas from its manufacture could have been factors in the amount of ink and acid deposited on these old papers. Writing on both sides of the paper must also be taken into account when comparing values in Table II.

Additional information was desired on the effects of solidly inked areas such as capital letters and blacked-in figures which contain large deposits of ink. To reproduce this condition, paper specimens were soaked for 30 seconds in inks A6 and B6. After aging, the embrittlement of specimens soaked in ink A6 was so great the fold test was impossible to make. The acidity was very high and could be expected to produce holes in the paper in the course of time. Again ink B6 was less acid and held up better in the fold test. Results of these tests can be found in Table II, column 3.

The acid present in these inks does not evaporate but spreads into the fibers adjoining the ink strokes. Evidence of this sometimes can be found in blank leaves which have been in contact with a written page. A light brown writing will appear in reverse on the blank sheet and can be read by holding it to a mirror. A test on an eighteenth century specimen of such a sheet did not reveal the presence of iron, which would have indicated a transfer of ink. Since the area containing the brown writing in reverse was more acid than the clear margin (clear margin pH 5.0, reversed writing area pH 4.8) it was concluded that this discoloration was due primarily to the migration of the acid in the ink to the blank sheet. In this connection, both Mitchell and Waters give information on the spreading of sulfates in writing.

The research of Zimmerman, Weber, and Kimberly indicated that copperas is injurious to paper, but gum arabic, tannic and gallic acids show no adverse effect on it. With the exception of the solvents, no further test seemed necessary on the basic ingredients of these old inks. Besides water, as before stated, wine was often used to dissolve the compounds for making ink, while beer, ale, and vinegar were only occasionally specified. Two inks, one made with wine and the other with vinegar instead of distilled water, contained the same proportions of ingredients as ink A6. After aging, the folding endurance was decreased to a greater degree than that of inks made with distilled water. The acidity was also higher, but the ink made of wine had a tendency to decrease in acidity on aging, due probably to the volatility of the organic acids of this solvent. These data may be found in Table IV.

TABLE IV

	Date of Paper	Uninked	Distilled Water	White Wine	Vinegar
% Retention Folding Endurance	1770	97	65	50	57
	1722	96	55	43	45
pH Control	1770	6.6	5.2	4.5	4.9
pH Heated	1770	6.6	5.0	4.7	4.8

The foregoing experiments have pertained to those factors in inks which have had an adverse effect on paper. However, the paper of a few documents of this period is uninjured by the ink with which they are written and there are quite a large number in which only a relatively small amount of damage had been done. Documents No. 5 and 7 in Table II, appeared to be in excellent condition, bearing no indication that the ink had been injurious. As a whole, the brown inks found in the survey as well as in Table II did not exhibit discoloration or injury to the paper to the degree effected by black inks. Tests were made to obtain additional information as to the possible factors which have influenced this condition.

Ink powder made by evaporating the ink to dryness on a water bath and then adding distilled water to its former volume showed less tendency to damage the paper than the original ink. The acidity was also less, perhaps due to a very small amount of the mineral acid being volatile. The ink powder made from ink B6, the type that soon turns brown, showed but relatively little damage to paper on aging. The results of these tests can be found in Table III, column 4.

All inks of the period were not necessarily as concentrated as inks A6 and B6. Several formulae of Table I specified less ingredients than those in inks A6 and B6, one having only 1½ g. of copperas per 100 c.c. of solvent. Many scribes wrote with a narrow quill point, sometimes using spring water to mix their powders. Spring water or river water is often alkaline, due to the presence of bicarbonate of calcium. These factors would be reflected in the final acidity of a document. Table V contains inks A 1½ and B 1½ which were compounded at one-fourth the concentration of inks A6 and B6. The ink powder was made as formerly. Distilled water, containing 200 parts per million of calcium carbonate to simulate the water of a spring, was used to dissolve the powders. The lines were drawn in ratio of one inked to seven uninked spaces to represent writing done with a narrow point quill. The results are interesting, proving the fact that ink of lower concentration does only slight injury to paper on aging and possesses little acidity. The ink powder showed no decrease in folding endurance and almost no increase in acidity. These seem to be some of the factors governing inks that were not particularly damaging to paper. A narrow quill point and a light deposit of ink are obviously two primary reasons why specimen 5 in Table II is in such excellent condition today.

TABLE V

	Date of Paper	Uninked	Inked	Ink Powder
INK A 1½				
% Retention Folding Endurance	1722	96	89	99
	1799	101	88	102
pH after aging	1722	7.6	7.4	7.5
	1790	6.8	6.4	6.5
INK B 1½				
% Retention Folding Endurance	1722	96	95	93
	1790	101	85	99
pH after aging	1722	7.6	7.5	7.6
	1790	6.8	6.4	6.4

The results of this study indicate that nearly all of the iron gall inks were damaging to paper due primarily to their acidity. It is known that this acidity does not evaporate but continues to be active, weakening the cellulose structure of the paper fibers. A procedure recommended by the writer in the AMERICAN ARCHIVIST, July, 1943, for neutralizing acid in paper was tried on specimens inked with inks A6 and B6. This consisted of soaking the documents for twenty minutes in lime water, (calcium hydroxide), then for the same length of time in a solution of 0.15% calcium bicarbonate. This not only neutralized the acid, but precipitated into the fibers calcium carbonate which has a stabilizing effect on the paper. This calcium carbonate also acts as a buffer against the absorption of any acid at a later time. The inked samples gave satisfactory results as is shown in Table III, column 5. These papers did not lose in folding endurance after aging and were mildly alkaline. There are a number of institutions now using the process prior to the lamination of deteriorated documents. Adelaide E. Minogue, formerly of the National Archives, recommends soaking in distilled water to remove this acidity, but states that highly acid and brittle documents can not be treated due to their disintegration in the bath. This difficulty may be overcome by using woven wire cloth or some other suitable means of conveying the documents in and out of the solution. Since all but two of the papers in Table II are far below the minimum standards for permanent papers, and specimens 1, 2, and 3 are among the most acid papers recorded, it is obvious that some method should be employed to eliminate this acidity.

Even though most of the manuscripts of these two centuries have been damaged in varying degrees by the acidity of the inks, we are indebted to the early inkmakers for selecting materials and formulae that have, in nearly all cases, remained legible either in a black or brown state. Considering their lack of scientific information and the tools then available, they did a good job. These brown inks have caused some alarm, the belief being that this change from black to brown was an intermediate step to complete obliteration. This does not necessarily seem to be true as both the old black and brown inks have become more inert, requiring stronger reagents to bleach than does new ink. Inks A6 and B6 were diluted ten times with distilled water and the writing of each was exposed to sunlight. Ink B6 soon turned brown, A6 gradually turned grey, and both eventually faded completely about the same time. The amount of ink deposited on the paper is a factor in how quickly the characters will be obliterated on long exposure. The deposit of ink on most of the early manuscripts was heavy, producing a good depth of color in the writing. This can be attributed to the concentration of the formulae used as well as to the practice of drying the ink with sand. Today part of the ink is often removed by blotting. In an attempt to obtain specimens of faded ink, two heavily brown inked eighteenth century manuscripts were exposed to several months sunlight, but the results were very disappointing. A thin deposit of ink will fade more quickly. Even though these inks appear to be relatively stable, it is inadvisable to frame valuable documents, as light is injurious to both ink and paper. If documents containing either brown or black ink are stored in darkness under good atmospheric conditions there seems no reason for fear of further fading.

This study has shown that iron gall inks were used almost exclusively in this country during the seventeenth and eighteenth centuries. As a rule, the inks which remained black were far more acid than those which had turned brown. Nearly all the early manuscripts tested were much higher in acidity than the maximum permitted in paper selected for permanent records. Test data has indicated that this acidity has been a large factor in the deterioration of many early documents. Manuscripts that will be of value to future historians should have this acidity eliminated if they are expected to be serviceable in years to come. To date, no reason has been found for concern over some of the black inks turning brown, the residual iron compounds appearing to be relatively stable if placed under good storage conditions.

The subject of iron gall inks of the colonial period is too broad to be covered fully in an article of this length. The data here presented may be of value to the archivist in understanding existing physical conditions of manuscripts as well as determining the best methods for their preservation. Additional investigation is in process and it is hoped that other workers will join in this field of study, thereby adding to the knowledge of the components of documents.

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