Now You See It...

A Brief Timeline and History of the Chemical Erasure of Iron Gall Ink

Barbara J. Rhodes, American Museum of Natural History Library

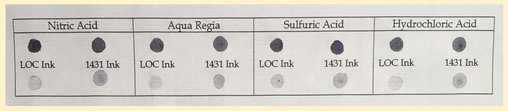
Introduction

The introduction of iron-gall inks, and of paper, made physical methods of ink removal, such as abrasion, less effective, so writers began to turn to chemistry to erase mistakes. Chemical ink removers were also used on written documents, books and prints, to remove stains, or to eliminate previous marks of ownership. Residual erasure chemicals such as acids and oxidizers can pose problems, affecting both text and substrate, for the conservator. This research surveys the recipes which were available for ink removal and the approximate dates of their use, in the hope that this information, and that provided by the experimental component, may prove useful in evaluating books, prints, and documents for possible treatment.

Recipes for chemical ink erasers started to appear around the 14th century in Europe, coinciding with the changes in writing materials. Conversely, the need for chemical removal of iron gall inks began to wane with the introduction of synthetic inks and ballpoint pens. Therefore, the scope of this brief history and timeline will be limited to developments in this subject from the late 14th century through the first few decades of the 20th century, as reflected in printed sources. I found some 922 recipes, consisting of 99 different single ingredients or combinations of ingredients (See the handout below). In some cases, what was counted as a recipe was simply a statement that a particular substance, such as lemon juice, could be used to remove ink. The most common types of ink erasers and their frequency of recommendation are shown in the table below. It was obviously not possible to review every ink removal recipe which has ever been published, and there are many sources which I have not seen. However, I believe that what I did find is representative of what is available; it should serve to help illustrate the trends in use of the various types of chemical removers for iron gall ink.

The Experimental Component

The experimental part of this research involved testing 24 of the most popular ink removal recipes on two different inks (See the "Recipes" handout below). The results obtained should be considered a "proof of concept" as to whether a particular ink eraser would indeed decolorize iron gall inks or not The test inks were used at half strength, as a weaker ink works better for demonstration purposes. The vegetable acids were used in saturated aqueous solutions, but the strong acids were diluted with water at a ratio of 1/5, as was recommended in the historic recipes. The juices were used straight, except for the sorrel, which was infused. Results are shown as sets of test dots of ink below control samples.



Strong Acids

The primary chemical ink erasers throughout history have been acids and oxidizers, with some use of alkali. The chemical ink removers discussed here, it should be noted, do not actually remove ink from the substrate. The acids discussed below operate via reduction, removing oxygen from the iron (III) oxide in the ink, and converting it to a colorless ferrous form.

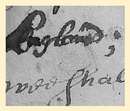
Nitric acid was the first strong acid specified to remove writing from paper; this recommendation appeared in the 1589 edition of *Natural magic* (Porta. 1589, 62), and replaced a previously published (1588) alchemical recipe (potassium nitrate and vitriol) for this compound. Nitric acid was the strong acid of choice for most of the late 16th through the 17th centuries, until it was eclipsed by hydrochloric acid. Part of the reason for this is the tendency of nitric acid to penetrate through the paper, and to leave a yellow stain (Godfrey. 1735, 109).

Sulfuric acid was observed to decolorize liquid ink in 1646 (Browne. 1646, 337), but was not mentioned specifically as an ink eraser until 1735 (*Dictionarium polygraphicum*. Vol. 2. 1735, D_3). It was somewhat less popular than the other strong acids, as it had to be used in concentrations strong enough to destroy the paper, and could also leave an oily stain (Haldat. 1802, 14). Nevertheless, it was still specified in some sources until 1856 (Champour and Malpeyre. 1856, 23-24).

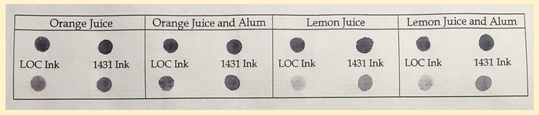
Hydrochloric acid (spirit of salt) was easily the most used of the strong acids for the purpose of ink removal. Its first appearance in this role was in William Salmon's 1673 *Polygraphice* (Salmon. 1673, 207), and it was frequently recommended until about 1909 (Morse. *Household discoveries* (Petersburg, NY: Success Company, 1909), p. 70. Hydrochloric acid was often specified in the context of removing ink from books and prints, though usually with the caveat that the vegetable acids were equally effective, and less likely to damage the paper.

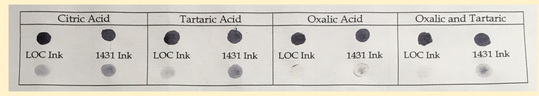
Strong acids were usually used in dilution, which eventually became more or less codified at a ratio of 5 or 6 volumes of water to one of acid, though the original strength of the acids can only be guessed at.

A 17th century chemical erasure.



The same erasure under IR, showing disruption of the paper surface.

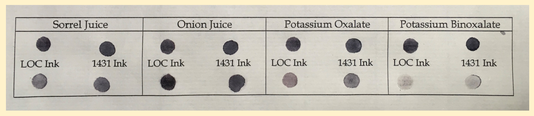


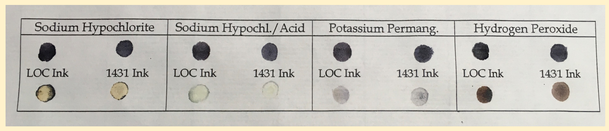


Vegetable Acids

The earliest vegetable acid to be used for ink removal is citric acid, obtained from oranges and lemons, and sometimes mixed with alum. Citric acid *per se* was not found until 1801, in William Henry's *Epitome of chemistry* (Henry. 1801, 215-216); it was used by itself or with other acids until the early 20th century. The other vegetable acids included tartaric, acetic, and oxalic acids, though acetic acid was not usually recommended on its own, but rather in combination with other acids or with chlorine compounds. The vegetable acids are reducing agents as well as chelating agents, combining with the iron in the ink to form soluble ferrous compounds. Tartaric acid, also first specified in Henry's *Epitome*, was used in several combinations -- with alum, citric acid and oxalic acid, but was most often recommended without additions.

The juice of wood sorrel (*Rumex acetosa*) was used for ink removal from the late 18th through the mid-19th century, but, after its mention in Henry's *Epitome* in 1801, its refined form, oxalic acid, was to dominate the ink removal scene until the end of the iron gall ink era. When combined with potassium carbonate, it formed potassium oxalate and binoxalate, both of which were also widely used. It was sometimes suggested that oxalic acid should be boiled in a tin spoon before use, as the presence of tin facilitated the decomposition of metallic oxides ("Procedes pour enlever les taches sur les livres et les estampes," *Bull. Arts All.* 4:391). Tin (II) chloride is a reducing agent; by itself it does not seem to have been recommended specifically for ink stains on paper until 1857 (*Inquire within*. 1857, 62), though it was not unpopular thereafter. It was often used with vegetable acids, especially oxalic and acetic.





Oxidizers and Alkali

One of the most effective oxidizers of iron gall inks is chlorine, which is also a strong base; the same is true of compounds such as calcium or sodium hypochlorite. (Alkali as such do not seem to be effective in decolorizing iron-based inks, though quicklime was tried repeatedly.) The first suggestion that chlorine could be used for removing ink from paper appears in 1787, in Jean-Antoine Chaptal's observations on the new bleach (1787. Chaptal. "Observations sur l'acide muriatique oxigéné." *Hist. Acad. Roy. Sci.* 611-616). Early methods of producing chlorine involved reacting hydrochloric acid with manganese, or with red lead (minium). In 1806, Samuel Parkes included in his *Chemical catechism* a statement that "Half an ounce of red-lead being added to three ounces of common muriatic acid, will render it fit" for removing ink stains from prints and old books (Parkes. 1806, 229). This process continued to be recommended for ink removal until at least 1856 (Pilkington. 1856, 186), and for bleaching prints until 1873 (*Facts and hints*. 1873, 312).

One widely used ink remover consisted of a solution of chloride of lime (calcium hypochlorite) and acetic acid, which also liberated chlorine; this was available either as a single mixture, or in two separate bottles, applied sequentially. By the 1890s, the "two-liquid" chlorine-evolving ink erasers came to feature borax, which was added to one or both components. Both these types of recipe were repeated well into the 20th century.

From about the middle of the 19th century onward, other oxidizers have been suggested, such as hydrogen peroxide, ozone and potassium permanganate. Ozone was first tried as an ink remover in 1861 (1861. "The Use of ozone for cleaning books, removing ink, etc." *Mech. Mag.* 75(1861):37); recipes featuring potassium permanganate began to be used by bookbinders at the beginning of the 20th century (Cockerell. 1901, 72), and continued into the 1930s. Both ozone and potassium permanganate have been shown to cause damage to paper, and they are not generally used by conservation professionals; indeed, ozone is now considered an atmospheric pollutant.

Few of the chemicals described above would be considered suitable for use in treatments today, though there are some, including hydrogen peroxide and calcium hypochlorite, which, if used with suitable precautions, are still of service.

Carter's Ink Eradicator, one of the popular two-solution ink removers of the 20th century.

TIMELINE OF INK REMOVAL

The table below depicts the timelines for 20 chemical ink erasers, beginning with recipes found in two 15th century manuscripts. The types of ink removers are listed below the table in numerical order based on the first year in which they were published. The table is divided by decade of publication, with an indication of the number of times in each decade an ink removal recipe of a particular type was found. Only recipes which were found 10 or more times were included. As it was not feasible to find and include every edition of every work, it seemed most informative to simply indicate trends.

	Ms.	1530	1550	1560	1570	1580	1590	1600	1610	1620	1630	1640	1650	1660	1670	1680	1690	1700	1710	1720	1730	1740	1750	1760	1770	1780	1790	1800	1810	1820	1830	1840	1850	1860	1870	1880	1890	1900	1910	1920	1930	1940
1	1		5	9	2	4	2	2	11	1	1	2		2	2		1	1					1				1	1															
2	4			6		2			5						2	4	2		2								1	4	3	5	2									6	1	2	
3	1			2		3	2		2	1				2		4		1					1				1	1														
4	1		6	8		5	2		4	3		1	1	5	1	1	2	1					1		1		1	1														
5			1	4		5	3	1	5	1	1	2	1	3	1	1	1	1					1				1	1										1				
6				1		4	2		1	2	1			1	1	4	1	1			1	1	1	1	2	2	3	1			1		1		1							
7						2	2		1		1	4	2	7		4			2		1			2	3	2	5	6	2	4					1	1						
8													1								1					1	1	2	3				1									
9															1	1					2	1					1	7	9	13	5	1	1		6	5	1	3				
10																										2	3						3	1	1	3	4	9	1	1		
11																										1		3	10	13	9	3	7	1	3	1	4	1				
12																											2	7	4	8	4	4	4	1	8	18	11	6	8	2		1
13																												6	4	11	4	3	2		4	3	2	2	3			
14																												7	4	8	4		2		4	3	3	2	1			
15																												2		2	2				2	2		2	2			
16																													2	1		1		1	2	5			1			
17																														1				1		4	6	3	1	1		
18																																	1		2	3	2	1	3			
19																																			3	9	9	5	9	1	1	1
20																																				1	5	3	9	1	1	

1. Potassium Nitrate and Vitriol, with variations 1398-1801
2. Citrus Juice (with alum variations) 1398-1939
3. Gem Salt, Common Salt, and Alum 15th c-1750
4. Fig Juice and Ceruse 15th c-1801
5. Salt Alkali and Sulfur 1558-1907
6. Rabbit Flesh and Quicklime 1566-1871
7. Nitric Acid 1589-1884
8. Sulfuric Acid 1658-1856
9. Hydrochloric Acid 1673-1909
10. Alum, Amber, Potassium Nitrate, and Sulfur 1787-1920
11. Chlorine 1787-1907
12. Oxalic Acid 1791-1940
13. Citric Acid 1801-1912
14. Tartaric Acid 1801-1912
15. Potassium Binoxalate 1809-1908
16. Potassium Oxalate 1810-1916
17. Sodium Hypochlorite 1827-1920
18. Tin Chloride 1858-1915
19. Calcium Hypochlorite and Acetic Acid 1872- 1940
20. Citric Acid and Borax, then Calcium Hypochlorite and Borax 1887-1920

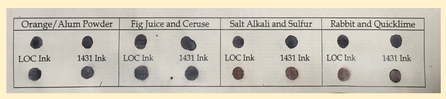
Distillation by alembic.

Alchemy and Ink Removal

While many early ink removal recipes relied on natural ingredients such as acidic fruit juices, alchemical formulas for solvents, requiring a controlled heat source and distillation equipment, were often recommended as well. For example, nitric acid was first described around 1300; the formula included vitriol, potassium nitrate, and alum, distilled together (2002. Karpenko. "Some notes on the early history of nitric acid," *Bull. Hist. Chem*. 34:106). This solvent formula, specified for the removal of ink, appeared among Jehan Alcherius' compiled recipes (Merrifield. 1849, 46). It could be strengthened by the addition of ammonium chloride, which would have produced "aqua regia," a mixture of hydrochloric and nitric acids.

The Carmelite brother Domenico Baffo compiled a long list of ink erasers, one of which was to be distilled from rock salt, common salt, alum, and ammonium chloride (1906. Mazzi. "Del modo di comporre l'azzurro oltramarino," *Riv. Bib. Arch.* 17:46); this combination of ingredients closely resembles a recipe from the 10th century which produced hydrochloric acid (Taylor. 2015, 229). Baffo's recipe was widely repeated until at least the late 17th century.

Another early solvent recipe which seems to have been widely known featured a distillation of Roman vitriol, mercuric sulfide, and salt (Multhauf. 1966, 161-162). This formula was adopted by Paracelsus in the 1530s for removal of ink (Waite. 1. 1894, 358), and was also repeated in numerous sources for centuries. Girolamo Ruscelli specified a similar ink removal recipe in the 1559 *Secretes of the Reverende Mayster Alexis of Piemont*, which also included a like composition called the "Mother of all waters, for to make all metalles liquifiable." This metal solvent was prepared from equal parts of potassium nitrate and vitriol, distilled together, to which was added another mixture, of mercury and sulfur (Ruscelli. 1559, 16b, 69b-70). Though Paracelsus' recipe specifies Jamen (Yemen) alum rather than salt, this specific form of alum was often confused with rock salt, so it appears probable that he was following alchemical sources. Whether these or the recipes cited above were used by anyone other than serious experimentalists is perhaps debatable, especially as much simpler preparations would have been easily available.



Aldrovandi's rabbit.

Powdered Ink Erasers

The earliest powdered ink eraser recipe, dating to 1398, consisted of powdered alum mixed with orange juice to form a paste, then dried again (Merrifield 1849, 62). Curiously, I did not find this powder recommended after the early 18th century, until 1912, at which time the recipe specified citric acid and alum (1912. "Ink eraser." *Nat. Drug*. 42:316). Fig juice mixed with ceruse (lead carbonate) seems to be the next oldest ink eraser powder; it was one of three specified by Baffo, including the orange and alum recipe, plus one which featured garden plants, dairy products, and quicklime. The fig and ceruse powder was made by kneading the ingredients into a paste, allowing it to dry, and repeating the process three or four times, adding new fig juice each time. After this, the mixture was reduced to powder again, and was ready for use (1906. Mazzi. "Del Modo di Comporre l'Azzuro Oltramarino." *Riv. Bibl. Arch*. 17: 46). This recipe was repeated in numerous publications until at least 1801. It does seem capable of at least discoloring ink, due to the vegetable acids in the figs.

An erasive powder was introduced in 1558, in *Natural Magic*, which consisted of little pills of "salt alkali" (probably potassium carbonate) and sulfur (Porta. 1558, 64). These were to be rubbed over the writing until no vestige remained; the recipe was repeated many times until the beginning of the 19th century, and made a last appearance in 1907, in which the recipe calls for sulfur and "any alkali" (Gros 1907, 774).

My favorite of the ink eraser powders was made from dried and powdered rabbit meat mixed with quicklime. The rabbit meat served no real purpose, except perhaps as an abrasive; the quicklime was the only active ingredient. This recipe was first published by Antoine Mizauld in 1566 (Mizauld. 1566, 27b), and it was published all over Europe; Ulysses Aldrovandi even included it in his discussion of rabbits as a species in his monumental volume on quadrupeds (Aldrovandi. 1637, 381). By the 18th century, it is mostly found in French works, with its last mention in 1871 (Bloquel. 1871, 356).

The most popular eraser powder, called "radirpulver," did not make an appearance until 1787, in two separate German publications (Halle. 1787, 152; *Das goldene Buch*. 1787, 448-449). It contained equal amounts of potassium nitrate, sulfur, alum and amber, powdered finely together. The active ingredients worked by oxidation of the ink; the amber does not seem to have contributed much, though it does contain succinic acid, and it also had an abrasive quality. This recipe seems to have been exclusively German until the latter half of the 19th century, when it began to appear in pharmaceutical journals, ending with a surge in interest during the late 19th and early 20th century.

Notes

Aldrovandi, U. 1637. *De Quadrupedibus Digitatis Vivparis Libri tres.* Bologna: Apud Nicolaum Tebaldinum.

Bloquel, S-F. 1871. *Les Mille et Un Amusements de Societe* Paris: Delarue.

Browne, T. 1646. *Pseudodoxia Epidemica.* London: Printed by T. H., for E. Dod.

Champour et F. Malpeyre, F. 1856. *Nouveau Manuel Complet de la Fabrication des Encres* Paris: A la Librairie Encyclopedique de Roret.

Chaptal, J.-A. 1787. "Observations sur l'Acide Muriatique Oxigné," *Histoire de l'Academie Royale des Sciences.* 611-616.

Cockerell, D. 1901. *Bookbinding, and the Care of Books.* London: John Hogg.

Dictionarium Polygraphicum. 1735. Vol. 2. London: Printed for C. Hitch, and C. Davis.

Godfrey, B. 1735. *Miscellanea Vere Utilia*. London: Printed for J. Robinson.

Das Goldene Buch fur Menschen. 1787. Leipzig: In der Schonfeldschen Handlung.

Gros, H. 1907. *Criminal Investigation.* New York: The Lawyers' Co-Operative Publishing Company.

Haldat, C. N. A. 1802. *Recherches Chimiques sur l'Encre.* Nancy: Chez J.-R. Vigneulle.

Halle, J. S. 1787. *Magie, Oder die Zauberkrafte der Natur.* Vol. 1. Wien: Gedrucht ben Johann Thomas Edlen von Trattnern.

Henry, W. 1801. *An Epitome of Chemistry.* London: Printed for J. Johnson.

Inquire Within for Anything You Want to Know. 1858. New York: Dick & Fitzgerald.

Karpenko, V. 2002. "Some Notes on the Early History of Nitric Acid," *Bulletin of the History of Chemistry*. 34: 106.

Mazzi, C. 1906. "Del Modo di Comporre l'Azzuro Oltramarino, Trattatello di Frate Domenico Baffo." *Rivista delle Bibliotche e degli Archivi.* 17: 31-50.

Merrifield, M. P. 1849. *Original Treatises on the Art of Painting*. Vol. 1. London: John Murray.

Mizauld, A. 1566. *Memorabilium, Utilium, ac Iucundorum Centuriae Novem.* Paris: Apud Fredericum Morellum.

Morse, S. 1909. *Household Discoveries.* Petersburg, NY: Success Company.

Multhauf, R. P. 1966. *The Origins of Chemistry.* London: Oldbourne.

Parkes, S. 1806. *A Chemical Catechism for the Use of Young People.* London: Printed for the Author.

Pilkington, J. 1856. *The Artist's Guide and Mechanic's Own Book.* Boston: Sanborn, Carter and Bazin; Portland: Sanborn & Carter.

Porta, G. *Magiae Naturalis, sive de Miraculis Rerum Naturalium, Libri IIII.* Naples: Apud Matthiam Cancer.

Porta, G. 1589. *Magiae Naturalis*. Naples: Apud Horatium Saluianum.

"Procédés pour Enlever les Taches sur les Livres et les Estampes." 1845. *Bulletin de l'Alliance des Arts.* 4: 391.

Ruscelli, G. 1559. *The Secretes of the Reuerende Maister Alexis of Piemount.* Translated by William Ward. London: s.n.

Salmon, W. 1673. *Polygraphice* 2nd ed. London: Printed by E. T. and R. H. for R. Jones.

W., A. H. 1873. *Facts and Hints for Every-Day Life.* London, Paris, and New York: Cassell, Petter, & Galpin.

Taylor, G. M. 2015. *The Alchemy of Al-Razi. A Translation of the "Book of Secrets."* CreateSpace Independent Publishing Platform.

"The Use of Ozone for Cleaning Books, Removing Ink, etc." 1861. *Mechanics' magazine* 75: 37.

Waite, A. E. 1894. *The Hermetical and Alchemical Writings of Aureolus Philippus Theophrastus Bombast, of Hohenheim, called Paracelcus the Great.* Vol. 1. London: James Elliott and Co.