ADVANCES IN THE FORENSIC ANALYSIS AND DATING OF WRITING INK

ABOUT THE AUTHORS

Richard L. Brunelle has a bachelor's degree majoring in chemistry obtained from Clark University in Worcester, Massachusetts and a masters of science degree majoring in Forensic Science obtained from The George Washington University in Washington, DC. Most of his career was spent with the Bureau of Alcohol, Tobacco and Firearms (ATF), where he retired in 1988 as Chief of their Forensic Science Laboratory with 28 years of government service. After retirement from ATF, he established and operated Brunelle Forensic Laboratories for ten years, where he specialized in the dating of inks on questioned documents.

During his career, Brunelle published approximately 50 scientific publications, including a textbook on the Forensic Examination of Ink and Paper, a chapter in a Handbook of Forensic Sciences, and a chapter in an Encyclopedia of Forensic Sciences. He was the recipient of the John A. Dondero Memorial Award, presented to him by the International Association for Identification for developing the first capability in the United States for dating inks. He also established the Society of Forensic Ink Analysts (SOFIA), which was incorporated in Virginia in 1997. This was the first professional association in the world for forensic ink chemists.

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By

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and

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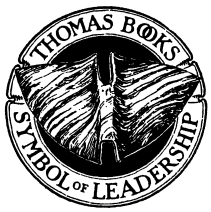

CHARLES C THOMAS • PUBLISHER, LTD.
Springfield • Illinois • U.S.A.

Published and Distributed Throughout the World by

CHARLES C THOMAS • PUBLISHER, LTD.
2600 South First Street
Springfield, Illinois 62704

ISBN 0-398-07346-5 (hard)
ISBN 0-398-07347-3 (paper)

Library of Congress Catalog Card Number: 2002020460

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Printed in the United States of America
MM-R-3

Library of Congress Cataloging-in-Publication Data

Brunelle, Richard L.
Advances in the forensic analysis and dating of writing ink / by Richard L. Brunelle and Kenneth R. Crawford.
p. cm.
Includes bibliographical references and index.
ISBN 0-398-07346-5 (hard) -- ISBN 0-398-07347-3 (pbk.)
1. Writing–Identification. 2. Ink. I. Crawford, Kenneth R. II. Title.

HV8076 .B78 2002
363.25'65–dc21 2002020460

Dedicated
to the Memory of
Dawn Marie

PREFACE

The dating of documents has become a valuable tool for the detection of fraud. Ink dating chemists in the federal government, and in the private sector, routinely conduct examinations of documents submitted in connection with a wide variety of criminal and civil investigations.

The reasons these examinations have become so important is simple–they provide conclusive proof of fraud, when it exists–and a strong case for authenticity, when there is no evidence of fraud. Ink dating techniques have been instrumental in resolving many headline criminal investigations, such as the investigations of former Vice-President Spiro Agnew; the Howard Hughes (Mormon Will); the mass murderer, Juan Corona; and Watergate. The Mussolini and Jack the Ripper diaries were also proven to be frauds by ink dating.

Many civil cases do not make the headlines, but they often involve millions, if not billions of dollars. Ink examinations have been performed on documents in connection with numerous patent disputes, such as the patent for the manufacture of acid and stone washed jeans, the patent for certain video games made by Nintendo and Atari, and the invention of the laproscope. Medical malpractice, altered wills, divorces, wrongful terminations, insurance fraud, sexual harassment, copyrights, labor-management disputes, and legal malpractice are all situations that routinely require the dating of documents. Therefore it should be no surprise that these advances are rapidly becoming known worldwide by forensic chemists, document examiners, and by law firms that routinely question the authenticity of documents.

This book describes in detail the many advances that have occurred in methods used to date inks on questioned documents, since the publication of *Forensic Examination of Ink And Paper* in 1984. Using the methods described in this book, forensic chemists interested in this

line of work will be able learn how to compare, identify, and date inks on questioned documents.

Document examiners, who are usually the first to examine a questioned document, will learn the capabilities that exist with respect to ink dating. This will enable them to advise lawyers, when ink dating examinations are appropriate. Lawyers will be better able to conduct direct and cross-examinations of ink dating chemists and university professors will have a useful text to use in their forensic programs.

I would like to take this opportunity thank my wife, Diane, for her love and support and for encouraging me to do something useful in my retirement. She is the one who had to tolerate my moods during the writing of this book. I thank my daughters, Desiree and Holly for their everlasting love and unqualified support of everything I have done in my life. I thank my grandchildren, Jason, Tina, Jake, and Sam, for their love and for adding so much more meaning to my life. My thanks also go to my new family, Jason, Andrea, Tim, and Chris for their love and sincere interest in my accomplishments. The love of Joe, my son-in-law, and Sue, my favorite partner in cards, is equally appreciated.

Tony Cantu provided much appreciated technical advice for this book as he has provided ink analysts for decades. His many published papers are cited as technical references in the following pages. Al Lyter is to be thanked for his contribution of known dated ink samples for some of the experiments first described in this book. In addition, his research is also cited more than once. Robert L. Kuranz and Dr. Ben Fabien are recognized for providing technical review of the chapter on ink chemistry.

Lastly, my sincere thanks go to Erich Speckin who contributed some of the illustrations in this text. More importantly, I thank him for taking up the profession of forensic ink dating, which will help provide longevity to the profession I have loved for over 30 years.

R.L.B.

INTRODUCTION

The forensic examination and dating of documents is important in our society, because documents are used throughout our lives to record everything we do. It starts with our birth certificate and ends with our death certificate. In between birth and death, there are receipts, leases, deeds, contracts, checks, wills, sales agreements, promissory notes, loans, medical records, and yes, even tax returns. The validity of all of these documents is often questioned during litigation. In fact, no other instrument of crime is as prevalent in our society as the document. Newspapers and the media report rapes, murders, bombings, kidnappings, fires, and other violent crimes. Yet, crimes committed with documents involve billions of dollars annually and actually have a bigger impact on society than do violent crimes.

Since the development of the first ink dating capabilities in 1968,[1] there have been many advances in this field. Now, not only can the first date of manufacture of an ink be determined, it is also possible to determine when an ink was written on a document. As a result, federal and local law enforcement agencies are routinely relying on these techniques in their criminal investigations. In civil areas, lawyers call on ink dating specialists in the private sector to date documents involved in a wide variety of cases. Such cases involve medical malpractice, altered wills, patent disputes, divorces, tax fraud, stock fraud, insurance fraud, discrimination, sexual harassment, wrongful terminations, labor-management disputes, copyright cases, and a wide variety of contractual disputes.

Documents may contain several items that can be chemically analyzed for dating purposes. These items include writing inks, paper, correction fluids, photocopy toners, laser printer toners, ink jet printer inks, and typewriter inks. The most useful of these for dating purposes are writing inks.

The Forensic Examination of Ink and Paper,[2] published in 1984 by Charles C Thomas, Publisher, provides a complete description of methods used to analyze and date inks and paper at that time. That text also covers the historical development of writing inks and their chemical properties, manufacturing processes, writing instruments, printing inks, typewriting inks, and paper manufacturing processes. Since this text endeavors not to overlap *The Forensic Examination of Ink and Paper*, readers should be familiar with the contents of that book before reading about the advances described in this text.

This text describes the advances that have occurred since 1984 for the chemical comparison, identification and dating of writing inks, as well as discussion of new writing inks that have been developed. Advances in the dating of inks are primarily in the area of relative age comparisons (ink dryness measurements) and the accelerated aging of inks. These methods involve comparing the relative dryness of questioned inks with known dated inks of the same formulation, stored under the same conditions and written on similar paper. Accelerated aging of inks can be used to date inks, when known dated inks are not available. Both of these methods measure rates or extents of extraction of the inks with weak and strong solvents. Some methods measure only the volatile components of inks.

We have not covered the examination of paper in this text because few advances have occurred in this area. In addition to detailed descriptions of new laboratory techniques, we will present actual case examinations and results. We will discuss Court admissibility of the methods according to the Frye and Daubert rules, as well as the establishment of a new professional association dealing with forensic ink examinations, The Society of Forensic Ink Analysts (SOFIA).

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1. Brunelle, R. L. & Pro, M. J.: A systematic approach to ink identification. JAOAC, 55: 823, 1972.
2. Brunelle, R. L. & Reed, R. W.: Forensic Examination of Ink and Paper. Springfield, IL, Charles C Thomas, 1984.

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HISTORICAL DEVELOPMENT: HOW WE GOT HERE

BACKGROUND

To appreciate the current state-of-the-art of the forensic comparison, identification, and dating of inks, it is necessary to acknowledge the pioneering work done by our predecessors in this field.

Their accomplishments have paved the way for the techniques that are in use today. The most significant early work in the comparison of fountain pen inks was Mitchell's *Inks: Their Composition And Manufacture*,[1] published in 1904. Mitchell updated this work in 1937, when he published another book with the same title.[2]

While numerous articles were published on the differentiation of inks, only a few researchers published procedures for dating inks. Witte[3] described the early work of Hess, Mitchell, and others for the dating of fountain pen inks. These studies were done about 1930 and involved the relative aging of inks using ion (chloride and sulfate), migration, fading, and extractability.

Witte developed techniques for removing microdiscs of ink on paper for chemical analysis in 1963. In 1968, Brunelle developed a similar microplug sampling technique. His procedure used a 20-gauge hollow-point needle and syringe to remove ink from documents. These developments were important because, for the first time, chemical tests could be performed on the ink without significant damage to the documents examined.

Research on methods to compare inks rapidly increased, beginning about 1950. Paper chromatography,[4] thin-layer chromatography,[5] electrophoresis,[6] chemical spot tests,[7] gas chromatography,[8] high-per-

formance liquid chromatography,[9] and infrared spectroscopy,[10] were all used for the comparison of inks. Eventually, thin-layer chromatography became the method of choice for comparing inks, because of its simplicity, reliability, and low cost. In the early 1960s, Werner Hofmann with the Zurich Cantonal Police Laboratory, used a standard ink reference collection to identify and to determine the first date of manufacture of ballpoint inks.[11] He used paper chromatography, TLC, spectrophotometry, spot tests, and the usual non-destructive tests to compare and match questioned and known inks.

All of the above accomplishments paved the way for Brunelle to establish the first systematic approach for the identification and dating of inks in the United States in 1968 at the Bureau of Alcohol, Tobacco and Firearms. He compiled a comprehensive Standard Ink Reference Collection, consisting of inks manufactured throughout the world.[12] By comparing the dye compositions of questioned inks with the standard inks, he was able to identify the questioned ink and determine when that ink was first manufactured. This was the beginning of ink dating as it is known today in the United States. This ink reference collection was transferred from ATF to the United States Secret Service Forensic Laboratory upon Brunelle's retirement in 1988. The Standard Ink Reference Collection is the largest in the world and now consists of over seven thousand different formulations of ink.

DATING OF FOUNTAIN PEN INKS

Mitchell's 1937 book describes chemical tests on iron gallotannate inks to estimate their age. These tests were based on the color of blue-black inks and the speed of reaction of the inks with certain chemicals. The color tests required standards of known age. He compared the rate of disappearance of the blue color of questioned inks with the known dated standards. The chemical tests measured the effect of oxalic acid on the pigment iron gallotannate. Mitchell found that the black pigment in freshly written inks bleached immediately and the blue color spread over the paper when the ink was treated with oxalic acid. Older inks, three or four years old, reacted slowly to oxalic acid and the blue color did not diffuse over the paper.

Mitchell was probably the first researcher to experiment with the dryness of fountain pen inks on paper. He theorized that the iron gal-

lotannate first formed is readily soluble in dilute acids. As oxidation proceeds, a resinous tannate is slowly formed until the tannate ink becomes insoluble in the dilute acids.

Kikuchi's research provided the basis for the solvent extraction techniques in use today for estimating the age of writing inks. She reported this work in 1959.[13] Her technique measures the time it takes for blue-black inks to disperse on paper when solvents are applied to the ink on paper. Kikuchi noticed that newer inks dispersed more quickly than older inks.

In 1984, McNeil reported the use of Scanning Auger Microscopy for dating manuscript iron gallotannate inks.[14] His method is limited to historical documents because the accuracy is limited to plus or minus about 22 years. The technique measures the outward migration of iron atoms from the ink boundary along a fibril. The migration increases exponentially with the age of the iron gallotannate ink. The absolute dating of the iron gallotannate inks is possible because the procedure is not affected by temperature or humidity. This means it is not necessary to have standard inks of known age for comparison.

DATING OF BALLPOINT AND NON BALLPOINT INKS

Credit for the development of the first ballpoint pen in 1939 is given to Ladislao Biro. Marketing of this new pen in the United States did not begin until about 1945, when 50,000 pens were sold at Gimbel's Department Store in New York City.

Changes in the chemical composition of ballpoint inks have occurred since their early development. Knowledge of these changes–and when they occurred–can be used for dating purposes. The first ballpoint inks were made with oil-based solvents like mineral oil, linseed oil, and recinoleic acid. Around 1950, ballpoint inks changed from oil base to a glycol base. Oil-base and glycol-base ballpoint inks are readily distinguishable because oil-base inks are soluble in petroleum ether–if the ink has been on paper less than 5 to 10 years. With age, oil-base ink becomes completely insoluble in petroleum ether. Glycol-base inks are insoluble in petroleum ether.

About 1954, another change to the composition of ballpoint inks occurred. Chelated metalized dyes began to be used. The most frequently used of these dyes is the blue-green copper phthalocyanine