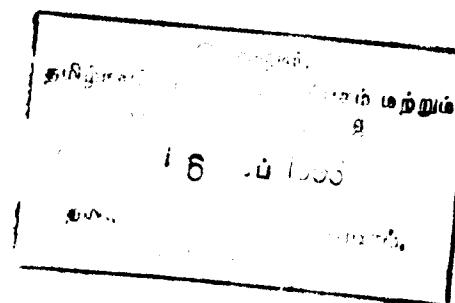


RESTAURATOR

International Journal for the Preservation
of Library and Archival Material

Volume 14 · Number 3 · 1993

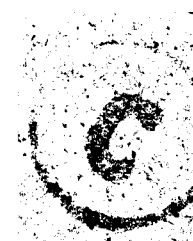


1330
93

MUNKSGAARD · COPENHAGEN

9581.02

Restaurator
1993.14.3
165121



A
VI 7085 m. 1993
1993.14.3
165121

Board of Editors

EDITOR AND EDITORIAL OFFICE:

Dr. HELMUT BANS, Elisabethstraße 23, D-80796 Munich 40, Germany.

ASSOCIATE EDITORS:

N. S. BAER, Professor, New York University, Institute of Fine Arts: Conservation Center, 14 East 78th Street, New York, NY 10021, U.S.A.
RICHARD D. SMITH, President, Wei T'o Associates, Inc., P.O. Drawer 40, 21750 Main Street Unit 27, Mateson, IL 60443, U.S.A.

CONSULTANT EDITORS:

GERHARD BANIK, Prof. Dr., Staatliche Akademie der Bildenden Künste, Fachbereich Restaurierung, Am Weißenhof 1, D-70191 Stuttgart 1, Germany.
ESTHER BOYD-ALKALAY, Chem. Eng. 17 Rehov Reiness, 53480 Givataim, Israel.
ALAN CALMES, Preservation Officer, National Archives and Records Administration, Washington, DC 20048, USA.
TOM COLLINGS, Senior Lecturer, Camberwell School of Art and Crafts, Peckham Road, London SE58 UF, England.
IAN COOK, Principal Conservator, National Library of Australia, Canberra A.C.T. 2600, Australia.
LORE E. FLEMING, Chief Conservation Officer (Eastern Pictorial Art), The British Museum, Dept. of Conservation, Great Russell Street, London WC1B 3DG, England.
FRANÇOISE FLIEDER, Directeur du Centre de Recherches sur la Conservation des Documents Graphiques, 36 rue Geoffroy-Saint-Hilaire, F-75005 Paris, France.
TOMOKICHI IWASAKI, Director, 1-13-4 Ueno Sakuraghi, Taito-ku, Tokyo, Japan.
Y. P. KATHPALIA, M.Sc., Scientific Officer, National Archives of India, New Delhi 5, India.
GABRIELLA KUNSZERI-ALBRECHT, Dr., Chem. Eng., Chief, Restoration Dept. of the Hungarian National Archives, Bécsi kapu tér 4, H-1250 Budapest 1 Pf. 3, Hungary.
ANNE LIENARDY, Rue de l'Orme 50, B-1040 Bruxelles, Belgium.
VICKI HUMPHREY, Manager of Paper Conservation, ARTLAB Australia, State Conservation Center of South Australia, 70 Kintore Avenue, Adelaide 5000, South Australia.
I. P. MOKRETSOVA, Dr., VNIIR, 10, Krestyanskaya pl. SU-109172 Moscow, Russia.
ROBERT C. MORRISON, Conservation Consultant, Contekk, P.O.B. 34, Narrabundah ACT 2604, Australia.
YULIA PETROVNA NYUKSHA, Dr. (biol.sc.), Chief of the Department of Hygiene and Restoration of Books, M. E. Saltykova-Shchedrin State Public Library of St. Petersburg, SU-191069 St. Petersburg, Russia.
GALINA S. ROZKOVA, Dr. (biol.sc.), Chief of the Department of Hygiene and Restoration of Books, State V. I. Lenin Library, SU-101000 Moscow, Russia.
ANDRÉE SCUFFLAIRE, Dr. Phil. L., Conservateur, Archives Générales du Royaume, B-1000 Bruxelles, Belgium.
NORMAN J. SHAFFER, Chief of Photoduplication Service, Library of Congress, Washington, DC 20540, U.S.A.
CHANDRU J. SHAHANI, Research Officer, Library of Congress, Washington, DC 20540, U.S.A.
ECKHART STRÖFER-HUA, Dr., Chemist and Chemical Consultant, Karl-Kunz-Weg 9, D-68163 Mannheim-Neustadt, Germany.
ANTONIO ZAPPALÀ, Director, Chemical Laboratory of the National Institute of Graphic Arts in Rome, Professor in Book Restoration at the University of Udine, Via della Lungara 230, I-00165 Roma, Italy.

RESTAURATOR, *International Journal for the Preservation of Library and Archival Material* is published quarterly. Subscription price 1993: DKK 720.00 including postage (USD 114.00), payable in advance. **Important** – for subscriptions delivered to addresses within the European Community. If you have a VAT registration number, you must provide this. Otherwise, please add your local VAT on journals to the above price in DKK: Belgium 6%, Denmark 25%, France 5.5%, Germany 7%, Greece 4%, Ireland 21%, Italy 4%, Luxembourg 3%, the Netherlands 6%, Portugal 5%, Spain 3%, UK 0%. Prices are subject to exchange-rate fluctuations.

Subscription orders may be placed with:

Head office:

MUNKSGAARD International
Publishers Ltd.
35 Nørre Søgade
Postbox 2148
DK-1016 Copenhagen K, Denmark
Tel: +45 33 12 70 30
Fax: +45 33 12 93 87

or *Regional office in USA:*

MUNKSGAARD International
Publishers Ltd.
238 Main St
Cambridge, MA 02142-9740
USA
Tel: +1 (617) 547 7665
Fax: +1 (617) 547 7489

or with any bookseller.

Active Archival Housing

by MARK G. VINE & WILLIAM K. HOLLINGER

1330
— 93

INTRODUCTION

It was in the investigation of W. J. Barrow, who published six volumes of data in the 1960s, that the causes of inherent vice in paper deterioration were initially identified.¹ Increased deterioration rates of paper cellulose were determined to be the result of acidic reactions, which appeared to result from a variety of efforts to produce less expensive papers. Papers made from ground wood or unbleached fibers that contained lignin and the use of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) to adhere sizing (acid resins) to paper fibers were among the primary causes, although there were others of a similar nature. As these issues were isolated, commercial papers that display improved characteristics of permanence were developed for publishing, fine arts and records documentation applications. This was done in the context of traditional conservation treatments intended to remove or neutralize acids generated as papers deteriorate. Quality original-use papers are now frequently made in an alkaline process and include an alkaline reserve placed into the paper during manufacture.

Placing an alkaline reserve in original-use papers was thought to have resolved one aspect of a problem recognized and defined by earlier researchers. Subsequently, alkaline reserves were incorporated into housing materials as an extension of their role in original-use papers. Thus equipped, housing papers and boards, many of which had been previously subject to the same degenerative cycles as collections materials, would no longer exacerbate the problem of acidity.² At that time, the addition of alkaline reserves to housing components was largely corrective, designed to elevate the intrinsic archival properties of enclosure materials.

Subsequent development efforts of this company³ resulted in the introduction of boards designed specifically as structural elements for archival enclosures.

One such material, patented and introduced in the 1980s, is a triplex board in which the exterior layer is lignin and sulfur-free and contains a traditional alkaline buffering, the middle layer comprises a sheet of archival polyester and the other side of the board is a neutral pH, non-buffered and lignin- and sulfur-free paper. With the introduction of products such as this, modified boxboards with alkaline reserves were supplanted, in this case by a special-purpose archival housing board with inert enclosure surfaces designed to not exacerbate deterioration and barrier layers to interdict entry of harmful elements through the housing materials.

In the developmental sequence from equivalence to protection, the design criteria were that enclosure materials should be inert, inactive or chemically compatible with the collections they housed. Certain collections, photographic emulsions and protein-based textiles, for example, required storage in contact with pH-neutral surfaces without the alkaline reserves indicated for papers. In those cases, the reserves were omitted for the same reasons they were added for papers. The criteria were based on a dual concept of the archival enclosure: it would offer as much physical strength and barrier protection as possible and it would prove chemically compatible in contact with collections.

This model of the archival enclosure required that it provide some deterrence against external sources of degradation and would not itself contribute to the deterioration of collections. The new model, developed by the company presenting this report,³ provides active, preventive conservation within the enclosure. It controls and reduces oxidizing gases and their associated acid-based derivatives. Such oxidizing gases may be deteriorative byproducts of the artifacts themselves, or they may be external intrusions, including atmospheric pollutants, discharges from electrostatic copiers, peroxides emitted from oil-based paints or other recognized external sources.

In the presence of oxidizing gases, acids may be formed when moisture is present within the collection environment. Organic-based collections materials, including celluloses, dyes and other complex natural elements, are quite adversely affected by the presence of oxidizing gases. Inorganic collections materials that have naturally occurring reactions with oxidizing environments, in particular metals and mineral collections, can also be considered to be at risk.

Proper chemical filtration and recirculation of the air within a building may accommodate general environmental influences, but the products of inherent vice within collections housings will not be adequately controlled by physical plant design. Similarly, the more effectively sealed the housing, in the innocent service of providing a barrier to external elements, the more concentrated the deteriorative elements in the environment within.

The introduction of a new model of conservation housing, one that can

actively contribute to the preservation of collections, represents a significant conceptual departure in the role of the archival enclosure, and opens a new field of inquiry in preventive conservation.

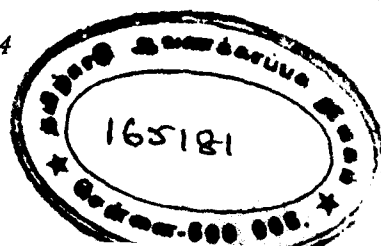
STRUCTURE

The new product is called MicroChamber™. The papers of this type consist of three or more discrete component layers of 0.10 mm. The boards consist of seven or more layers with a total thickness of 1.5 mm or more.

The transmission surface of MicroChamber™ paper designed to face collections is manufactured with a specific porosity to permit exchange between the internal, active layers and the interiors of collections enclosures. The active layers contain proprietary mixtures of specific activated carbons and alkaline buffers in papers of precise porosities, which function as a trap to neutralize oxidizing gases and their associated acids (Fig. 1). The exterior layer is an alkaline buffered, alkaline pH, sulfur-free and lignin-free conservation paper.



Fig. 1. Scanning electron micrograph of one of the active layers of MicroChamber™ paper. Within the fiber activated carbon coated with alkaline buffering (white) is dispersed.



A
V1:885m,N93
N92.14.3

The layers are formulated to be interdependent in the overall performance of the material.

ACCELERATED AGING

Independent laboratory tests have been performed on MicroChamber™ and conventional housing papers. The test parameters were both externally introduced elements, oxidizing gases and in protocols where the primary deteriorative elements were internal: the byproducts of paper degradation in accelerated aging. These tests indicate a synergistic relationship between the alkaline buffers and the specific activated carbons which, in proprietary mixtures, are components of the active layers of MicroChamber™ housing papers.

In one test of protective enclosures for vintage book papers during accelerated aging, samples of a 30-year-old book paper were enclosed in various housing materials and subjected to 88 hours of accelerated aging at 100°C, after which they were TAPPI-conditioned for more than 26 hours and tested for residual folding strength. The results are values expressed in units of the MIT fold at 1 kg of load. The final results are given in Table 1.

The 30-year-old paper stored in MicroChamber™ B housings exhibited sufficient strength to withstand an average of 15.1 folds. The same paper housed during the test in acid-free, lignin-free alkaline-buffered alpha cellulose enclosures was able to withstand an average of only 6.9 folds. Samples of the same paper housed in commercially available conventional manila file folders withstood an average of 5.1 folds. These test results indicate a greater differential in the strength retained between the book papers aged in MicroChamber™ and traditional alkaline buffered housings than between those papers aged in buffered and acidic housings.

Tests using a paper that had already aged for 30 years under natural conditions indicated a significant differential in results based on which enclosure material had housed the samples. Initial manufacturer's tests, using the same test protocols with new alkaline book papers, had previously shown a similar differential in residual strengths. Together, the results of the two tests indicated that residual strength varied in similar proportions, with both new papers and papers already well into the natural aging cycle, depending on which archival material was used for the enclosure.

HYDROGEN PEROXIDE INCUBATION TEST

Another standard test of MicroChamber™ products was completed by an independent testing laboratory specializing in photographic materials. The

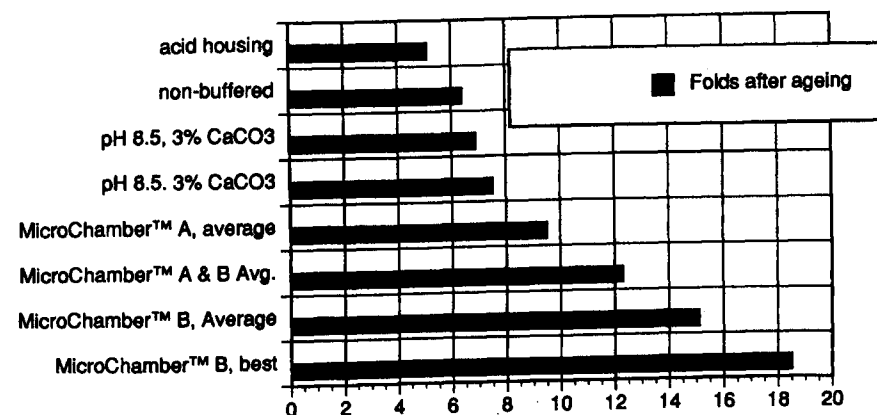


Fig. 2. M.I.T. folding endurance of the paper of a 30-year-old book aged for 88 hours at 100°C in different housings:

1 MicroChamber™ B	best result	18.5
2 same	average	15.1
3 MicroChamber™ A and B	average	12.3
4 MicroChamber™ A	average	9.5
5 conventional buffered (3% CaCO ₃) lignin and sulfur-free housing paper	best result	7.5
6 same	average	6.9
7 conventional neutral non-buffered lignin and sulfur-free housing paper	average	6.4
8 conventional manila folders	average	5.1

hydrogen peroxide incubation test used to evaluate silver photographic image stability is described in ANSI Standard IT 9.15-1992. The test environment is a two-litre desiccator in which monitor emulsions, covered by samples, are subjected to 2000 parts per million hydrogen peroxide for 18 hours at 50°C and 80% relative humidity.

The archival housing samples were tested with respect to their ability to protect the monitor material, an archivally processed microfilm. The use of microfilm as test monitor for the general class of processed commercial photographic materials is based on the observed deterioration of these materials⁴ and because microfilm also provides a sensitive monitor for the detection of undesirable components within the test materials themselves.

Fine-grain silver, dispersed in a gelatin binder and processed to archival standards, has proven a sensitive material for the detection of oxidizing gases. Various studies into the redox blemishes on processed microfilm stored in low-quality cardboard boxes that emitted peroxides as oxidizing gases have appeared in the literature.⁵⁻⁷

The same redox reaction was found to be active when researchers tested processed photographic film placed into a recently painted room where oil-based paints had been used. The curing oil-based paints included large volumes

Active Archival Housing

of oxidizing gases, particularly peroxides, which resulted in the formation of redox blemishes in the image.⁸

The significance of the formation of these redox blemishes on the general silver image can be particularly appreciated with microfilm, which contains a very high density of information confined to a small area. On microfilm, redox blemishes invisible to the naked eye can result in the complete obliteration of letters and even words. The protocols of the test produce Draconian conditions, and the parameters for failure, an 0.05 image density increase on the monitor emulsion, will identify even small quantities of reactive gases penetrating the housing materials. Any product sample that can secure the monitor emulsion under the conditions of ANSI IT9.15-1992 will provide a safe environment for the storage of peroxide-sensitive collection materials.

Test results, reported as changes in silver-image density, are measured by light transmission densitometry through a blue filter, because redox silver deterioration is yellow in color.

Samples not protected by the test material receive full exposure to the testing environment. The image becomes badly degraded and the visual information contained within the microfilm is largely converted to the yellow redox blemish form. If a non-buffered conservation paper is used for protection, the surface area available for reaction is reduced. Samples protected in this way might be defined as showing slightly reduced damage, but generally there is no difference to non-protected samples. A buffered conservation paper provides a clearly better protection. Greater areas of overall grey tonality of the image instead of yellow are the evidence that the presence of an alkaline reserve within the paper reduces some of the redox reaction. Nevertheless, it must be stated that there is significant damage, i.e., yellowing. Only samples protected by a MicroChamber™ product are not affected by the testing.^a

Regarding the density numbers, no change was observed in all samples protected by a MicroChamber™ product. All other samples show increases (i.e., image deterioration) between 0.3 and 1.6.

CONCLUSION

The formulations and fiber structures for the MicroChamber™ papers vary because there are conflicting tasks to be performed. The interior layers must readily accept, capture and neutralize deleterious by-products of deterioration that form as artifacts age, while the exterior layers must keep oxidative and

^a Color photographic prints demonstrating the test results are available upon request from the authors.

acid gases in the surrounding atmosphere at bay. To help achieve this, fiber selection and structure differs throughout the paper structure. Activated carbons can be selected that, when combined with alkaline buffers, are effective against many of the deleterious compounds we wish to capture and neutralize. For the compounds against which activated carbon is not effective, we use a group of alkaline buffers in which pores and molecular cages sized to capture specific molecules have been fabricated. Traditional alkaline buffers must be used with both the activated carbon and the special buffers containing the molecular traps.

Microchamber™ papers are generally composed of multiple, non-laminated layers of paper, which are comprised of a variety of paper fibers, differentially processed and specifically selected to produce the maximum efficiency and performance in the MicroChamber™ paper. Within these layers are traditional alkaline buffers with either activated carbons and/or alkaline buffers specially modified with miniature interconnecting, multidimensional passageways (sized and shaped to accommodate specific molecules), leading to tiny molecular cages, where unwanted molecules of a deleterious nature are captured and neutralized. The efficacy of the various MicroChamber™ papers and boards is based on the interrelated functions performed by the structural components, molecular traps and neutralizing buffers together. We did test activated carbon used without alkaline buffers in conservation quality paper, and the performance was essentially identical to the performance of traditional lignin and sulfur-free alkaline buffered paper.

SUMMARIES*Active Archival Housing*

W. J. Barrow was the first to identify an alkaline reserve as a main parameter of paper permanence. Subsequently, relevant compounds were not only incorporated into quality original-use paper but also into housing materials. Further development concentrated on the structure of such materials, on their porosity, and on specific activated carbon together with the alkaline compound. Recent tests have demonstrated a highly superior protection given by relevant housing materials.

Conservation active de documents d'archives

W. J. Barrow a été le premier à identifier la réserve alcaline comme un facteur essentiel de la permanence du papier. Par la suite des substances appropriées ont été non seulement incorporées dans le papier support du document mais aussi dans les matériaux de rangement. Les développements ultérieurs se sont concentrés sur la structure de tels matériaux, sur leur porosité et sur la

présence de charbon actif spécifique avec un composé alcalin. Des tests récents ont montré la protection nettement supérieure donnée par des matériaux de rangement appropriés.

Konservierungsaktives Aufbewahrungsmaterial

W. J. Barrow hat zuerst das Vorhandensein einer alkalischen Reserve als wesentlichen Parameter für die Dauerhaftigkeit von Papier entdeckt. In der Folge wurden entsprechende Substanzen nicht nur zur Herstellung von Papier verwendet, das als Informationsträger dient, sondern auch von Papier bzw. Karton für Schutzhüllen. Die weitere Entwicklung konzentrierte sich auf die Struktur solchen Materials, auf seine Gasdurchlässigkeit und auf die Anwesenheit von spezifisch aktivierter Kohle zusammen mit der Puffersubstanz. Neueste Tests haben gezeigt, daß ein entsprechendes Material einen Schutz geben kann, der dem von anderen Materialien weit überlegen ist.

REFERENCES

1. Barrow, W. J.: *Permanence durability of the books*, vols. 1-6. Richmond, VA: W. J. Barrow Research Laboratory, 1963-1969.
2. Slavin, J. & Hanlan, J.: *An investigation of some environmental factors affecting migration-induced degradation in paper*. *Restaurator* 13 (1992): 78-94.
3. Conservation Resources (UK) and Conservation Resources Int., Cowley, Oxfordshire (UK) and Springfield, VA (USA).
4. Weyde, E.: *A simple test to identify gases which destroy silver images*. *Photographic Science and Engineering* 16, 4 (1972): 283-286.
5. Henn, R. W. & Wiest, D. G.: *Microscopic spots in processed microfilm: their nature and prevention*. *Photographic Science and Engineering* 7, 5 (1963): 253-261.
6. Henn, R. W., Wiest, D. G. & Mack, B.: *Microscopic spots in processed microfilm: the effects of iodide*. *Photographic Science and Engineering* 9, 3 (1965): 167-173.
7. McCamy, C. S. & Pope, C. I.: *Redox blemishes, their cause and prevention*. *Journal of Micrographics* 3, 4 (1970): 165-170.
8. Feldman, L. H.: *Discoloration of black and white photographic prints*. *Journal of Applied Photographic Engineering* 7, 1: 1-9.

Mark G. Vine
Conservation Resources (U.K.)
Unit 1 & 4, Pony Road
Horspath Industrial Estate
Cowley, Oxfordshire, OX4 2RD
United Kingdom

William K. Hollinger, Jr.
Conservation Resources Int.
8000-H Forbes Place
Springfield, VA 22151
USA

The Setting of Modern Inks Before Restoration Treatments

by MARTINE LEROY & FRANÇOISE FLIEDER

INTRODUCTION

Facing a great quantity of documents to restore, research has been conducted for many years to mechanize various processes of restoration and to make them faster. The automation of leafcasting has been emphasized. The initial research was made during the 1950s at the National Library in Sofia by E. Alkalay¹ and later at the Saltykov-Shchedrin-Library in St. Petersburg by M. G. Blank and J. P. Nyuksha.² This technology has been taken up in several European countries and is now used worldwide.

The process consists of using paper pulp suspended in water and allowing it to deposit on the gaps thanks to a rapid flow of water. The grafts, however, do not always stick sufficiently to the document. We therefore tried to improve this technology ten years ago. We defined a certain beating degree to be necessary for leafcasting and we chose the best adhesive for the process.^{3,4}

One problem remained unsolved: how to fix water-soluble inks for the process.

BIBLIOGRAPHY

The inks of ancient manuscripts, ferrogalllic or carbon inks, are usually insoluble in water;⁵⁻⁷ this is not the case with most contemporary writing inks: felt-tipped pen, stylograph, etc. It is therefore necessary to fix them before leafcasting. In selecting the most suitable products for this purpose, their harmlessness to paper must be taken into consideration. Several publications describe different procedures to be used to fix clothes dyes.⁸⁻¹⁰ They are, however, not suitable for the problem of ink on paper, because there is a fundamental difference between dyed textiles and ink on paper. Textile dyes are inside the object,

whereas inks remain on the surface. Fixation processes must be very different. Very few articles deal with this particular problem. We mention M. G. Blank's² work, who proposed in 1963 the use of dicyandiamide and formaldehyde condensates. More recently K. Bredereck^{11 14} emphasized the importance of the ionic nature of dyes in inks, as cationic dyes stick better to paper than anionic ones. On the other hand, some acidic dyes fade in the presence of hydroxide ions, particularly in the aqueous deacidification process, almost instantaneously producing carbinols. The authors have analysed a great number of fixers to determine their fixing power and their effect on the tensile resistance of treated papers. The conclusions of this work show that different products (formaldehyde and dicyandiamide condensates; or polyhalides and polyethylene imines condensates; stearyl dimethylbenzyl ammonium salts) give good results. Nevertheless, the mechanism of ink fixation is still not well known.

CHOICE OF FIXATIVES

We worked with Sandoz products (Dermafix S, Indosol E 50, Tergotan GS, Sandofix WE) and with a product of Bayer (Tanigan LD) generally used for dye fixing (Annex).

A first selection was made on contemporary documents showing a great number of unstable inks. We then determined for each product their concentration, their time of immersion and the kind of drying that best fixes inks. We also examined deacidification action with magnesium bicarbonate on fixed inks.

We selected through this first study four fixatives: X321, Indosol E 50, Tanigan LD and Sandofix WE. The first three products are effective only on blue inks and the Sandofix WE on black, blue, red and green inks. That is why it was chosen for the following research. Sandofix WE is a polymer of dicyandiamide, formaldehyde and ammonium chloride.

The operational protocol is as follows: paper samples were immersed for one minute in a 10% Sandofix solution and then rinsed. Some of them were deacidified in a solution of magnesium bicarbonate, some not. Good ink fixing was obtained with both.

HARMLESSNESS TO PAPER

To verify Sandofix WE harmlessness to cellulose, we treated a 100% bleached chemical pulp and analysed its mechanical and chemical coordinates.

The following tests were chosen: mechanical characteristic variations (tensile strength, tearing strength, bursting strength, folding endurance and yell-

owing) and chemical characteristic variations (pH, copper number and viscometric degree of polymerization).

The results were obtained after and before accelerating aging (7 days at 90°C and 60% relative humidity) on Sandofix-treated papers with and without deacidification. The results are given in Table 1 and in Fig. 1.

It becomes evident that, before the accelerated aging, treated papers, deacidified or not, are not deteriorated, but we can notice the high copper number of the treated paper, which seems to be an anomaly. But after the accelerated aging process for samples that were not deacidified, we noticed a great loss of mechanical characteristics and also a high level of deterioration. The treated paper after deacidification does not present any alteration. Sandofix is totally compatible with paper when deacidification has been done. All these results have been confirmed on another kind of paper (newsprint).

STABILITY OF INKS TREATED WITH SANDOFIX

We worked with four stylograph inks (black, blue, red and green) marketed by Parker, Pelikan and Waterman. For each of them, lines were drawn on a 100% bleached chemical pulp. The samples were divided into three groups. One group used as a reference was not treated, another group was soaked for one minute in water, and the third group was immersed in Sandofix for one minute and then rinsed very well with water. The results were compared with the reference group.

Study of line profiles

A line profile is a luminosity curve of a definite vector; in this particular case it means a 15-mm segment perpendicular to the drawn lines.

They were filmed with a video camera and numerically analysed (Graftex-Optilab Software). For each sample, line profiles were elaborated and compared (Fig. 2). We analysed two types of information: the variability of the ink density (picks depth) and its migration during treatment (width of the points and base lines).

- Ink density variation: generally optical density of inks submerged in water containing Sandofix is not altered (except the green Waterman ink). The optical density of submerged and nonfixed inks decreased a lot (black and blue Waterman, blue Pelikan, all the green inks and most of the reds).
- Ink migration: after fixing with Sandofix, there is no more migration, but for other nonfixed inks we can observe that some picks have expanded and

Table 1. 100% bleached chemical pulp paper treated and not treated with Sandofix WE before and after accelerated aging

	Tensile strength (p)			Stretch to break (%)			Folding endurance			Tear (p)	
	variation (%)			variation (%)			variation (%)			variation (%)	
	CD	MD		CD	MD		CD	MD		CD	MD
Untreated	2215	5650		3.5	1.6		42	585		1159	1007
Treated	2190	5705	0	4.4	2.2	29	42	523	-10	1375	1052
Treated, deacidified	2175	5430	-3	4.4	2.3	31	40	626	6	1328	1125
Untreated, aged	2100	5525		3.5	1.7		26	272		902	1129
Treated, aged	1775	4590	-17	2.4	1.3	-29	12	43	-82	672	840
Treated, deac. aged	2065	5500	-1	3.1	1.8	-6	34	361	33	1023	1270

	Burst (kp)			Brightness			pH			DP _v			Copper number		
	variation (%)			variation (%)			variation (%)			variation (%)			variation (%)		
	CD	MD		CD	MD		CD	MD		CD	MD		CD	MD	
Untreated	2.15			86.2			5.95			840			0.51		
Treated	2.53	18		85.4	-1		5.45	-8		770			0.25		51
Treated, deacidified	2.70	26		84.0	-3		8.80	48		769			0.39		24
Untreated, aged	1.94			75.1			5.30			619			0.85		
Treated, aged	2.01	4		66.1	-12		5.10	-4		398			1.49		-75
Treated, deac. aged	2.40	24		73.5	-2		7.70	45		659			0.55		35

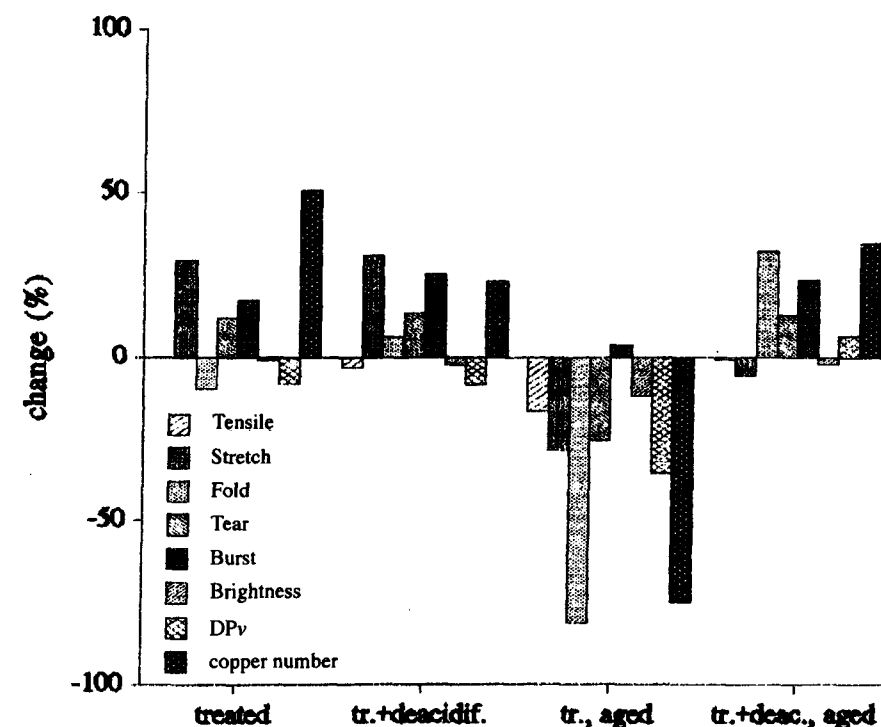


Fig. 1. Changes of some numbers characterizing the quality of paper and cellulose. DP: viscosimetric degree of polymerization.

that the baseline has changed in many cases. It shows that ink has spread on paper.

Ink colorimetric analysis

We conducted a colorimetric test with a Nanometric microspectrophotometer. Trichromatic coordinates were calculated with the CIELAB formula (chart L*, a*, b*); color differences are expressed by ΔE^* – color total difference – (Fig. 3) calculated according to the following equation:

$$\Delta E^* = I(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 I^{1/2}$$

We can observe for immersed inks in water a very high variation of ΔE^* (except for blue Parker ink), particularly for Waterman inks. This is usual because of the great solubility of those inks. For inks treated with Sandofix, ΔE^* variation is generally few (except for Waterman inks).

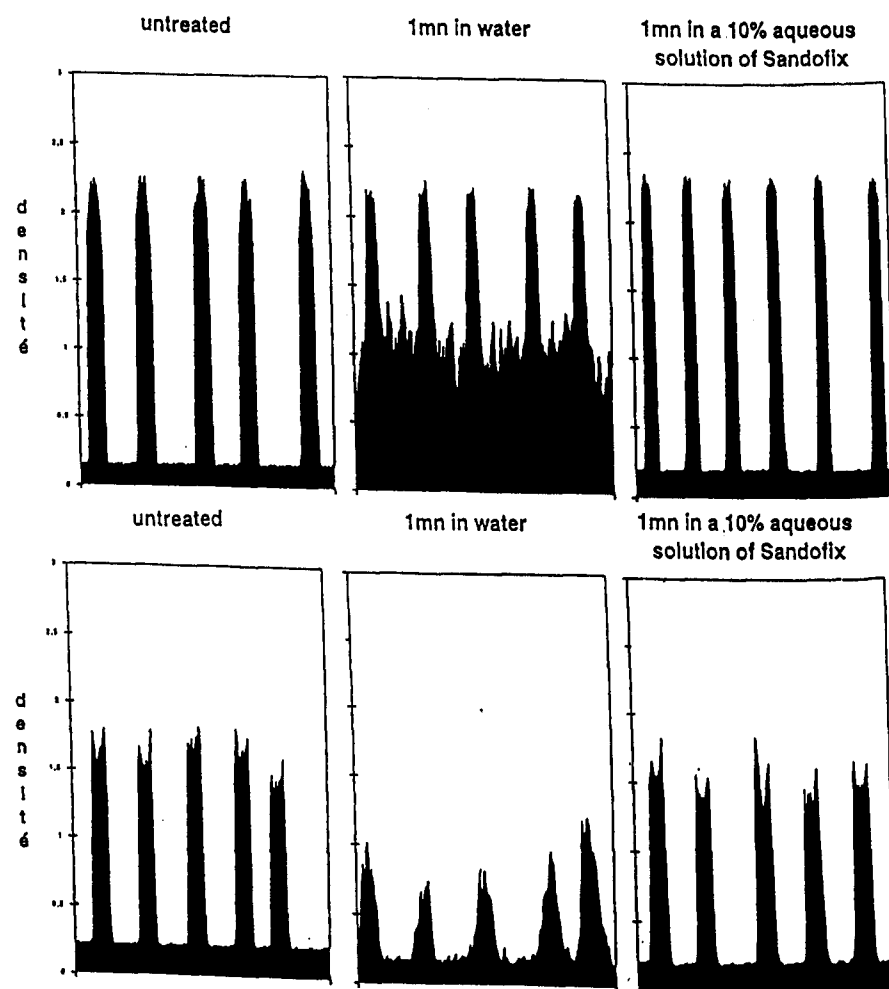


Fig. 2. Line profiles (cf., page 135) of black (upper) and green (lower) inks.

DISCUSSION

The results obtained show that Sandofix has rendered the experimental unstable inks completely insoluble without altering their color. Two assumptions could be made about this fixing mechanism: it could be an interaction between ink and Sandofix or just a deposit of a product looking like a film. This last assumption does not seem real because, during deacidification, rinsing the fixed document made the deposit go back into solution. On the other hand, as the aged and treated paper showed strong deterioration before deacidifica-

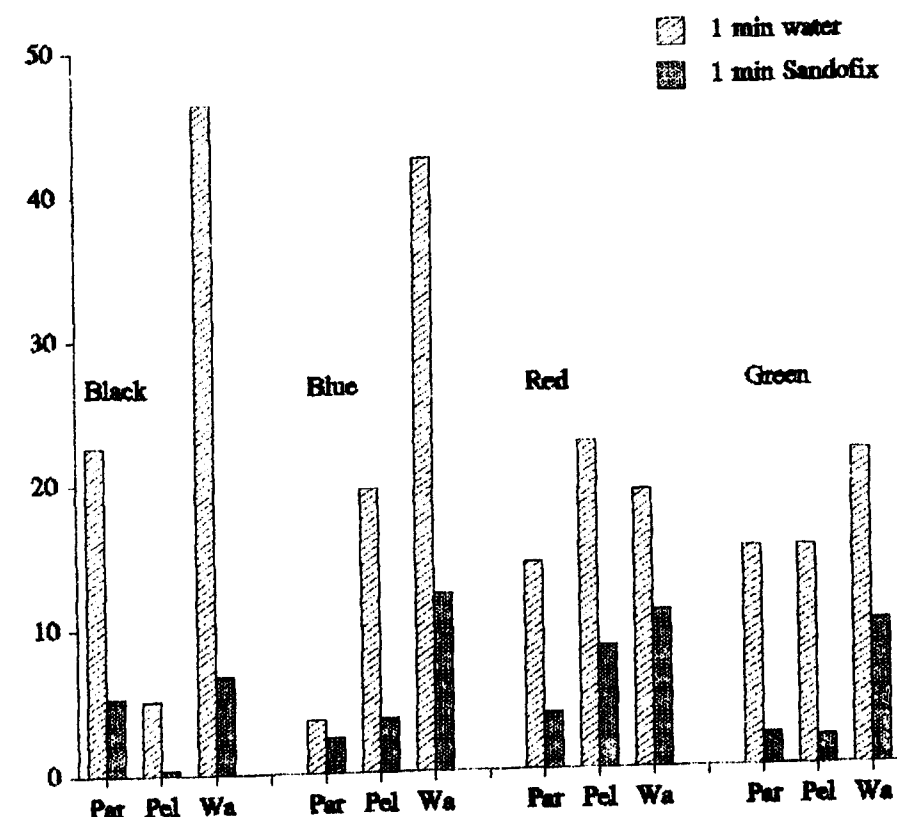


Fig. 3. ΔE^* variations (cf. the equation on page 135) of inks immersed in water and in a Sandofix WE solution (10%).

tion, we can conclude that Sandofix WE was entirely eliminated during the treatment with the magnesium bicarbonate. Grafts made on treated papers are good, but it would not be the same thing if the paper became hydrophobic.

CONCLUSION

It was necessary to find a solution to avoid unstable inks of some manuscripts to spread during all aqueous treatment. Here we have proposed a satisfactory solution for soluble inks in water, but nevertheless we have to resolve the problem of soluble inks in organic solvents.

These solvents are frequently used in restoration, particularly in some deacidification processes. Let's note that, for this type of ink, we can meet some difficulties.

Table 2. Ink density variations ΔE^* of inks immersed for 1 min in water and in Sandofix WE

	Untreated	Treated
Parker Black	22.66	5.28
Pelikan Black	5.08	0.33
Waterman Black	46.30	6.73
Parker Blue	3.66	2.41
Pelikan Blue	19.49	3.67
Waterman Blue	42.49	12.22
Parker Red	14.20	3.84
Pelikan Red	22.57	8.37
Waterman Red	19.08	10.73
Parker Green	13.06	2.21
Pelikan Green	15.11	1.94
Waterman Green	21.80	9.88

Sandofix WE does not harm cellulose with imperative treatment of deacidification before use.

ACKNOWLEDGEMENT

This work was realized with the financial help of the Archives Nationales. We are very grateful for their help.

SUMMARIES

The Setting of Modern Inks Before Restoration Treatments

The leafcasting of documents is more and more done in a mechanical way. As this operation is done in an aqueous area, some contemporary manuscripts containing unstable inks cannot be treated without an initial fixation. The aim of our research consists in choosing the best product by also ensuring its harmlessness to the paper. Sandofix was chosen.

La fixation des encres modernes avant des traitements de restauration

Le colmatage des lacunes avec de la pulpe des documents est de plus en plus souvent réalisé de manière mécanique. Etant donné que cette opération est réalisée en phase aqueuse, des manuscrits contemporains contenant des encres instables ne peuvent être traités sans une fixation préalable. Le but de notre recherche était de choisir le meilleur produit en tenant également compte de son innocuité sur le papier: le Sandofix WE a été retenu.

Das Festigen moderner Tinten vor einer Restaurierungsmaßnahme

Das Papieranfasern wird mehr und mehr in mechanisierter Weise durchgeführt. Da es sich dabei um ein nasses Verfahren handelt, können einige moderne handschriftliche Objekte, deren Tinte wasserlöslich ist, nicht ohne vorherige Fixierung bearbeitet werden. Das Ziel der Untersuchung war es, das bestgeeignete Fixiermittel zu finden, wobei es besonders auf die Unschädlichkeit für das Papier ankam.

TESTED PRODUCTS

Dermafix S (Sandoz). Aliphatic polyamine, polycationic; pH at 10% 6.94
 Indosol E50 (Sandoz). Aliphatic polyamine, polycationic; pH at 10% 6.92
 Tanigan LD (Bayer). Stearyldimethylbenzylammonium, cationic; pH at 10% 3.10
 Tergotan GS (Sandoz). Urea-formol precondensate, polycationic; pH at 10% 6.28
 X321 (CFPI). Stearyldimethylbenzylammonium, cationic; pH at 10% 6.15
 Sandofix WE (Sandoz). Methylolamide, cationic; pH at 10% 4.10

REFERENCES

1. Alkalay, E.: *Techniques de la restauration à la Bibliothèque nationale de Jérusalem*. ICOM Committee for Conservation. Triennial Meeting Madrid 1972. Preprint 4,1.
2. Blank, M. G.: *O zakreplenil chernil nykh tekstov*. In: *O sokhraneni bumagi, proizvedeni pechat i rukopisei*, 1963.
3. Leclerc, F., Flieder, F. & Bulle, F.: *Le colmatage mécanique des documents. Effet de l'incorporation d'un adhésif dans la pâte à papier*. In: ICOM Committee for Conservation. Preprints (8, 1987, Sydney). Los Angeles: ICOM, vol. 1, pp. 685-696, Group 14.
4. Leclerc, F. & Leroy, M.: *Le colmatage mécanique des papiers d'archives contemporaines*. In: *Nouvelles de l'ARSAG* (6 Juillet 1990) pp. 4-5.
5. Champetier, G. & Rabate, H.: *Chimie des peintures vernis et pigments*. Paris: Dunod, 1955, vol. II, chap. 27-28-29.
6. Coffignier, C.: *Couleurs et peintures*. In: *Encyclopedie de chimie industrielle*. Paris: Baillière, 1924, pp. 508-534.
7. De Pas, M.: *La composition des encres noires*. In: *Les techniques de laboratoire dans l'étude des manuscrits*, Colloques internationaux du C.N.R.S., Paris: CNRS, 1972, pp. 119-132, Extract.
8. Abeta, S., Yoshida, T. & Imada, K.: *Problems and progress in reactive dyes*. In: *American Dyestuff Reporter* 73, 7, (July 1984) 26-31, 49.
9. *Industrie chimique PCUK - Industries graphiques diverses*. In: *Information technique* 7913/F.
10. Richardin, P., Bonnassies, S. & Flieder, F.: *Étude du vieillissement de l'Elvamide 8061 utilisé comme fixatif des tracés pulvérents*. In: *Nouvelles de l'ARSAG* 2 (1986): 2-3.
11. Brederbeck, K. & Siller-Grabenstein, A.: *Die Möglichkeiten der Festigung von Farbstoffen und Tinten als Voraussetzung für die Restaurierungsmaßnahmen in Archiven und Bibliotheken*. In: "Internationaler Graphischer Restauratorentag", Berlin, 5-9 October 1987, p. 3.

12. Bredereck, K.: *Fixing of ink dyes as a basis for restoration and preservation techniques in archives*. Restaurator 9, 3 (1988) 113-131.
13. Bredereck, K. Blüher, A. & Siller-Grabenstein, A.: *Untersuchungen zur Fixierung von Schreibstoffen auf modernen Papieren als Voraussetzung für Restaurierungs- und Konservierungsmassnahmen in Archiven*. Das Papier 44 (1990) 137-146.
14. Bredereck, K. Blüher, A. & Siller-Grabenstein, A.: *Untersuchungen zur Fixierung von Schreibstoffen auf modernen Papieren als Voraussetzung für Restaurierungs- und Konservierungsmassnahmen in Archiven*. In: Conference on book and paper conservation. Abstracts, Budapest, 4-8 September 1990, pp. 129-130.

Françoise Flieder
Centre de Recherches sur la Conservation des Documents Graphiques
36 rue Geoffroy-Saint-Hilaire
F-75005 Paris
France

The Stability of Printing Inks

MARTINE MARAVAL & FRANÇOISE FLIEDER

INTRODUCTION

In recent years, many studies have been conducted to determine the qualities required to ensure the stability of paper. The aim of all this research has been to guarantee the best longevity to archive files. Based on this point of view, two questions remain to be clarified: what kind of printing inks can be used on permanent paper and what is the stability of such printed documents?

At the request of the Centre National de Lettres, we directed a study on printings on permanent paper. After briefly reviewing printing processes and ink composition, we present the structure and results of our research.

REVIEW OF PRINTING PROCESSES AND INK COMPOSITION

Printing has been known since the antiquity.^{1,2} Witnesses since 1000 B.C. emphasize that the Chinese knew already how to engrave and to print. By this time, inks were dyes in aqueous solution. They were called xylographic inks because they were used on carved wood. The oldest printings, kept to the present, date from the ninth century and came from China and Japan.

In Europe, printings on wooden boards first appeared during the fourteenth century. They were used for playing cards and later for religious pictures and texts. In about 1450, Gutenberg set up the industrial duplication of the mobile letter press process by running metallic alloys with lead and tin down the melting pots. New inks were elaborated: they were made from siccative oils, such as linseed or nut oils. The improvement of these technologies promoted printing all over Europe. During three centuries of its real rise, from the sixteenth to the eighteenth century, printing ink was made in printers' workshops by special workers called ink makers. Around 1818, Pierre Lorilleux achieved the mass production of inks, which were sold to printers. Since then,

The Stability of Printing Inks

industrial manufacturers have created many inks to fit to various new printing processes as well as numerous printing supports.^{3 5}

Before the most current printing processes are described, a rapid survey of all of them is necessary.^{6,7}

The printing processes

There are three different types of printing:

- direct printing with printing elements in contact with the support to be printed;
- indirect printing with an intermediary of transfer; and
- non-impact printing using computer memory (Annex 1).⁸

Direct printing processes

The letterpress process. The letterpress process requires a relief printing image carrier. A film of ink is applied to it using rollers. So high pressure allows the ink to be transferred from the face at the image carrier to the surface of the substrate. This technology was widely used until the middle of the twentieth century but at present is in decline.

The flexography process. This is a form of letterpress printing that uses flexible rubber or plastic plates and is mainly used for printing packaging materials.

The gravure process. This process is derived from two technologies of the fifteenth century: copper-plate engraving and etching. In this process the printing image is engraved into a metallic cylinder in the form of cells; the former are filled with ink. Printing is achieved by pressing the substrate between the gravure cylinder and an impression roller. Gravure printing is used primarily for long runs (more than 300,000 units) because of the expense of cylinders.

The silkscreen printing process. This is a stencil process. Ink is transferred to the substrate through a fine mesh of cloth, originally silk and nowadays synthetic fibers or metal threads. The stencil is treated in a way so that the areas not to be printed are impervious. Ink is then forced through the screen on to the paper. This process can handle any substrate and it is very versatile. It is used particularly for plastic containers, posters and point-of-sale materials.

Indirect printing processes

Offset lithographic printing. This process was created in about 1910 in the United States and based on a planographic system; it is derived from lithography, created by Senefelder in 1798, with direct contact between the porous limestone and the paper. Both technologies are based upon the repulsion of water and oil. Chemical treatment of printing plates permits ink to adhere to some areas (dry surfaces) and not others (wet surfaces). In the offset lithographic process, the ink image is transferred to a rubber blanket and then to the paper.

The di-litho process. This is used for printing some types of newsprint. It is like a letterpress rotary printing adapted to offset by adding a damping system. It is a transitional technology to support old equipment.

The dry offset process. This process, also called letterset, uses printing characters in relief with a transfer by a blanket.

Non-impact printing

Non-impact printing processes use computer memory. They include ink-jet printing and electrography. Printing can often be done by recording the data by computer, which allows quick modification during the production process.

The offset preponderance

Three processes currently share the largest part of the printing market (Fig. 1). Letterpress is mainly used for business cards, announcements, posters, etc. Gravure is more specific for long runs such as catalogs, colored magazines etc., because it is expensive and highly technical. For advertising and newsprint, the offset printing process is generally used. The equipment presents a wide variety of presses (from A4 cut size to the rotary 2 × 16 pages press that does 20,000 turns an hour).

Offset is known to be the best due to the following qualities:

- use in various quantities and sizes
- use with numerous substrates
- short time to get ready to run
- inexpensive.

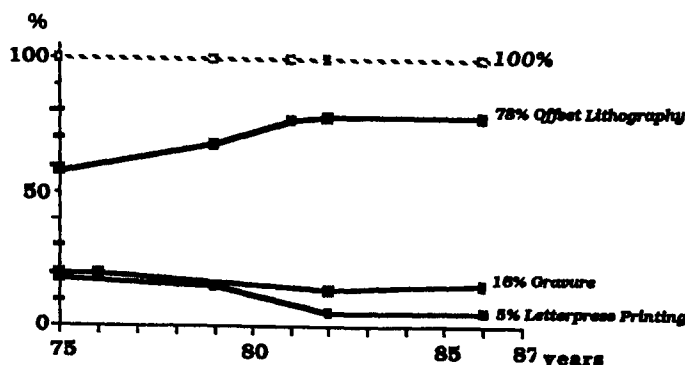


Fig. 1. Evolution of the main printing processes between 1975 and 1986 in France. Source: Durchon (8)

Nevertheless, offset remains a very peculiar process that requires extensive knowledge of technology and many steps.

After the text and pictures are laid out, printing is realized by exposure on the plate throughout the film. For the offset plates, it is usually composed with a light-sensitive diazo polymers on organic resins supported by an aluminum base. Hydrophobic image areas are defined on the plate. They have conserved the resin layer. The non-image areas are hydrophilic because they are composed of an aluminum oxide layer. The non-image areas are receptive to the aqueous damping solution, which rejects the ink towards the image areas.^{8,9} The plate is then fixed on a cylinder. A natural or synthetic rubber blanket (2 mm) mounted on a cylinder enters into contact with the plate and transmits the ink on the paper distributed in sheets or continuously (on reels).

Thanks to the blanket flexibility, this indirect printing process reduces wear by adapting pressures to the plate-blanket and blanket-substrate interfaces.

Color is reproduced in a four-color process. Colored images are printed by the succession of three colored inks: yellow, cyan and magenta followed by black ink for the darkest parts and the text. So four plates are exposed from an image realized through a filter eliminating the components which do not concern the studied color. Some machines have one, two or four colors; the latter allows the whole colored image to be printed at one time.

Offset ink components

Printing inks are more or less pronounced dispersions of pulverulent solids, i.e., pigments, in a liquid phase that is more or less viscous: the vehicle, also

called varnish or linker. They must usually produce very thin, flexible, adhesive films that dry very quickly.¹⁰⁻¹²

Ink = Pigments + Vehicle

While pigments are solid and discontinuous, the vehicle is assimilated to a continuous and liquid phase. So the vehicle is essentially used for transport and for binding the pigment particles to the paper.

Ink composition depends essentially on the printing process to which it pertains. The nature and the body of the varnish are determined by the type of machine used. It is the same for pigments, whose physical properties have to be adapted to the printing processes and to the expected result as well as the desired selling price.¹³⁻¹⁸ Nowadays most books are printed on offset presses either on sheets or on continuous rolls (Fig. 1). Our research is limited to the inks used for that printing process and to the study of the longevity of the realized records.

Offset inks are very viscous and usually dry according to the combination of two phenomena: penetration and oxidopolymerization.¹⁹

Three ink components will be studied: pigments, vehicles, and additives with special respect to the damping system.

Pigments

Pigments greatly influence printing quality. They intervene at several levels: the color (tint, intensity and brightness), the lightfastness and the resistance to external chemical and physical agents.^{20,21}

The main pigment qualities required for the offset process are:

- highest coloring power (because the ink film is very thin)
- inertia to water or to the damping solution
- inertia to peculiar drying (infrared, ultraviolet, oven)
- aptitude to develop the brightness.

They can be listed in three categories:

- black pigments
- white pigment
- colored pigments.

The black pigments are carbon black derived from the incomplete combus-

tion of natural gas or petroleum derivatives. They are ingredients of all printing inks.

The white pigments are divided into two groups according to their composition and their use: opaque pigments composed of titanium and zinc oxide and translucent pigments containing calcium or magnesium carbonates and aluminum hydrate. White pigments are among the components of many inks, used alone or to complete other pigments and to improve the stability and the visual qualities of the ink.

Colored pigments are divided into four groups:

- mineral pigments
- organic pigments
- lakes from fixed dyes on mineral support
- the toners, which are precipitates of derived dye salts.

Nowadays black pigments are made out of hydrocarbons. The old "channel" blacks are being replaced by new "furnace" blacks.^{20,22} Modification of the production process changes the structure of the carbon black particles. The brightness, the covering power and the running faculties of ink can be modified. The dispersion degree and the way that the pigment is covered influence the appearance, tint, hue, fluidity and brightness. For printing inks we use carbon black containing small particles (0.1 to 0.2 μm). In offset printing, their concentration is high and can reach 20%; moreover they must be bright and intense. They are sometimes used as oxide to improve the compatibility with the linkers and to increase their stability.^{21,23,24}

Sometime black inks have a blue tint to increase the contrast with white paper. Pigments added to the black help to resist acids, bases and oxidizing agents. If a more yellowish paper is used, such as in Germany or in England, yellow pigments are added to carbon black.

The dyeing materials used for colored offset inks are generally aromatic organic pigments. These pigmentary particles are bigger than carbon black and can have variable geometry (lamellas, spherical, circular or small plated).²¹

The vehicle

The main purpose of the vehicle is to carry the pigments and to allow them to be fixed on the paper.^{25,26} The variety of the vehicles depends strongly on the paper used. So newsprint offset inks are very fluid, because ink dries by penetration of the vehicle into the very porous paper. Non-covered pigments have a tendency to create dirt and spotting. For books, which need good

printing quality, the letterpress and offset processes use viscous inks. Their vehicle is highly film-forming, so they can cover the pigments and isolate them when the ink is dry. In this case the paper used is not very porous.

Thirty years ago, the highly viscous ink vehicles mostly contained linseed or wood oils: treated siccative oil, partly polymerized. Nowadays mixed polymerized vehicles are generally used. They are made of mixed synthetic or natural resins, spread in vegetable oil (mainly linseed oil) and not very viscous mineral oils. This composition favors the drying process on microporous paper by selective filtration followed by oxidopolymerization.

The additives

Offset inks have additives in the vehicles and pigments.²⁷ The drying process is controlled by dryers, mainly metallic compounds. Sometimes there are compounds to avoid the drying process of the ink on the blanket or the plate. The mechanical properties, viscosity, tack and brightness of inks can also be modified by using appropriate products (Table 1).

The damping solution

The damping solution highly influences the quality of the printing by separating the image and non-image areas. It is composed of water, buffer and additives. Water with a pH between 6.5 and 8 is generally used. The quantity of ions is controlled and must sometimes be reduced for HCO_3^- and CO_3^{2-} . Phosphoric buffers maintain the pH between 5 and 6. Additives are sometimes necessary, for instance, to change the surface tension (isopropyl alcohol), used as thickness reducers, antifungal compounds and also for ion sequestration (for Mg and Ca). In fact there is an emulsion of water in ink. Through a microscope we can see tiny drops when there is linked emulsion (good running) and a mixture of rough and tiny drops when there is a spontaneous emulsion (bad printing). Ink and water needs are nearly the same. The quantity of water brought on the paper by inks depends on the kind of the ink and plate.

Tests

Testing printing inks allows us to anticipate some behaviors and especially to find possible anomalies or inadequacies between the printing process, paper, ink and the required printing quality.³⁰⁻³⁴ In the different printing stages:

Table 1. Composition of offset inks. Source: Sirost^{20,25,26,29}

Inks components		% weight	Properties
Pigment	Carbon black (sometime bluish or yellowish) Organic pigments	15-20%	Color resistance
Vehicle	Hard resin	30%	Brightness
	- phenolic compound - modified colophan		Mechanical properties
	Solvent and diluent	45%	
	- petroleum compound - vegetable oil - glycerophthalic compound - high-molecular weight alcohol		
Additives	● drying initiator: esters with Co, Mn, Zr ● unpolishing compound: polyethylene wax, polyfluoro, silica, cornstarch ● gelling, anti-tack: bentonites, carbonates, organic compound with Al, polyamides ● water/ink emulsion: surface active compound, silicone, alcohol, amine	5-10%	Depending on the product

- before printing: viscosity, flow, tack, fly control, density, acidity, pigment homogeneity and flash point;
- during printing: printability, penetration, contrast (flatness and half-tone), picking and siccativity; and
- after printing: brightness, friction resistance, outline quality, flatness, density, lightfastness and chemical and physical resistance.

Printing ink manufacturers produce controlled inks. Usually, printers give them instructions and they choose the inks together. There are references on technical docketts, corresponding with national and international standards³⁵ (Annex 2):

- lightfastness: CEI 0259–NF Q 64002
Usually, black inks have a good resistance under light from 7 to 8.
- alkaline resistance: CEI 0559–NF Q 64005

Black inks do not especially resist alkalis (soda). Nevertheless, they are resistant in some series.

- solvent resistance: CEI 0459–NF Q 64004.

Ink producers usually emphasize alcohol and nitrocellulose, but it is especially useful to know whether the ink could be covered with an alcohol or nitrocellulose varnish. Generally they are adapted for special works: in every group of ink a varnishable equivalent is planned.

EXPERIMENTS

The great interest in book preservation and more generally for all printed records has inspired us to study the four inks used in four color systems: black, cyan, magenta and yellow. The chosen permanent paper corresponds with the usual printing type: 80 g/m³ in A3 size. Its permanence is assured by its composition: 100% bleached chemical pulp, sized with alkylcetene at pH 8–9, filled with 2% of CaCO₃ and some talcum. The manufacturer is Canson: Papier Barrière 80 g réf. 301.

In close collaboration with Ecole Française de Papeterie et des Industries Graphiques (EFPIG) in Grenoble, France, we considered 15 black inks and 11 colored inks produced by the main printing ink producers in France (Annex 3).

Tests before printing

Tests before printing allow us to examine the adequacy of ink and paper before printing on current presses; this also avoids any future incidents in the workshop. These tests were carried out with black ink and the permanent paper needed for future printing. Every black ink sample was characterized by:

- viscosity measurement; rigidity
- tack measurement
- printability tests.

Viscosity

Viscosity measurements of an offset ink could be realized by a classical means: a Laray viscosimeter. This tests the time it takes for an inked stick to fall through a slightly larger ring (Annex 4).

Tack

The tack is the strength necessary to separate a film. Although it cannot represent all phenomena produced during the printing on paper (especially the selective filtration), it determines the right paper for each ink: if the tack is very low, printing at high speed could cause ink fly, which means that some ink particles could fly in the printing workshop atmosphere. The tack measurement of an ink was done with a "tack-o-scope" (Annex 5). The results are given in Table 2.

Printability

Printability is the capacity of an ink to be printed on a given paper. Many methods and types of equipment have been used and improved during the last 30 years to obtain the required conditions on machines; some factors (such as the printing speed and the intervention of the damping solution) are not represented in the most commonly used printability test, but they provide interesting information about the association of paper and ink. In our case we used Prüfbau equipment, which runs with constant speed and pressure (Annex 6).

The drying time of an ink was verified from these printability tests, which

Table 2. Tack (cf. Annex 5) of 15 black inks

	Tack	Rigidity Dynes/cm ²	Viscosity Poises
A	194	1,000	240
B	120	5,500	165
C	164	15,000	285
D	166	7,000	305
E	106	15,000	330
F	124	8,000	255
G	132	8,500	160
H	164	9,000	340
I	144	9,500	250
J	170	10,000	300
K	142	16,000	250
L	148	7,000	470
N	86	3,500	140
O	140	2,500	250
P	170	18,000	400

gave precise indications about possible mackles and dirty marks during further printing (Annex 7).

All these preliminary tests allowed us to verify the compatibility of black ink samples with the paper chosen for our research. Viscosity and tack are good for offset use. Printability tests have shown that the 15 black inks selected are compatible with the chosen permanent paper and their drying time is quick enough to avoid the risk of mackles.

For colored inks, we did not do these tests, because the manufacturers have selected printable samples with the paper used on a classical offset machine. So, the printing was carried out on a current machine without changing the trading inks.

PRINTING

Printing was carried out on a press in Grenoble at the EFPIG with the 15 black inks and the 11 colored inks on Canson permanent paper.

Printing is composed of the different elements used in the offset process (Annex 10):

- flatness: a circle of 6 cm diameter, a strip in the grain direction and a strip in the cross direction
- a half-tone picture
- a graduated half-tone – from 10% to 100%
- a text
- control bars.

All these elements are gathered on an A4 film (21 × 29.7 cm).

The positive polychrome plate is exposed to the sun throughout the film under ultraviolet light for 3 min, then developed and finally fixed on a printing cylinder. Permanent paper sheets (Canson, papier Barrière 80 g réf. 301, A3 size 29.7 × 42 cm) are printed with the different samples of inks. After a minimum of 15 days of drying, the sheets of paper are cut up and can be studied. For every ink sample we printed 100 A4 copies. Every printed sheet was registered this way: a capital letter (A, B, C, ...Z) designating the ink used (Annex 3). It is index-linked with V after aging (AV, BV, CV, ...ZV).

Choice of accelerated aging

To study printed documents, we measured various properties before and after accelerated artificial aging. Two types of accelerated aging were used:

- damp heat aging: 30 days in an oven at 90°C and 65% relative humidity (RH). This high temperature was chosen after preliminary tests with black inks for 10 days at 60°C, 65% RH, which did not produce significant alteration.
- light aging: 300 h in an oven at 30°C and 50% RH under a 1500-W xenon lamp (radiant energy about 70 W/m²). These conditions allow significant degradation of blue bars (> 6th echelon; AFNOR NFQ 07-011 and NFQ 64-022). The aging of colored printing was followed by a kinetic study to examine degradation by regular sampling under high exposure (200 W/m²).

Choice of measurements

Many measurements were selected to control the effects of the accelerated aging of the printings on permanent paper. The results are taken from the averages before and after the different types of artificial aging.

Ink penetration

To characterize black printing, a new approach was taken towards ink penetration measurement on paper in close collaboration with Mr Baudin of EFPIG. The general principle is to compare the measurement on the overleaf of an inked sheet with the measurement on the front side throughout a white sheet. Reflectance values at 530 nm are measured with a reflectometer on an area of 10 mm².

Abrasion resistance

Tests were carried out on black flatness discs. The technology relies on the rotation of a printed sample against a white sheet, under different pressures, from 100 g to 400 g.

pH

To avoid a previous modification of the permanent paper acidity, pH could be measured by cold water extraction or a pH meter (TAPPI standard T 435 m 52). The permanent paper used has an alkaline filler, which gives a pH of about 9. This alkalinity could be influenced by the printing and the different types of aging.

Color

Color can be measured in two ways:

- on the black disc with a photometer, which records the trichromatic values (RX, RY, RZ). We can also obtain Y, which represents luminosity (if the tint fades, Y increases) and ΔE^* , is the total color difference (if the tint changes, ΔE^* increases); and
- on the entire area with a microspectrophotometer giving directly ΔE^* . It also provides the specific components of the colors L* and a*b*. L* refers to the lightness; a* denotes the degree of redness or greenness; b* indicates the degree of yellowness and blueness (Annex 8).

Optical density

Optical density is recorded with a reflection densitometer. The values are obtained with different filters according to the studied color:

- visible filter corresponds with the total density without a filter;
- blue filter to detect previous variance of density in yellows;
- green filter to detect previous variance of reds; and
- red filter to detect previous variances of blues.

Results

Black inks

Penetration. These tests do not allow whole inks to be classified according to their penetration degree. Nevertheless, some conclusions can be made. The ink E, with a low flatness density printing, is not very penetrating; the A, K and L samples have a high flatness density; the N and O ones are very penetrating. The others give more varied results. The results are very dependent on the pigment granulometry and the vehicle consistency. Furthermore, a high penetration of ink seems to be related to the longevity of the document, but it can sometimes bring visual problems with very pronounced print through vision; that phenomenon could harm the quality of legibility of the record.

Abrasion resistance. The abrasions on the flat surfaces have produced poor results, because of the heterogeneity of abraded surfaces. The high resistance of offset

Table 3. Black inks: color difference before and after accelerated aging

	Optical density without filter						L*	
	Damp heat aging				Light		Damp heat aging	light
	60°C		90°C		30°C		60°C	30°C
	DO	Variance	DO	Variance	DO	Variance	Variance	Variance
A	1.06		1.05		1.04			
A V	1.03	-3%	1.02	-3%	1.03	-1%	4%	3%
B	1.00		0.99		0.98			
B V	0.99	-1%	1.00	0%	0.98	-1%	2%	1%
C	0.99		0.97		0.96			
C V	0.98	-1%	0.96	-2%	0.94	-2%	2%	3%
D	0.98		0.97		0.98			
D V	0.96	-2%	0.96	-1%	0.97	-1%	2%	1%
E	0.89		0.89		0.89			
E V	0.88	-1%	0.88	-1%	0.88	-1%	1%	1%
F	0.96		0.95		0.96			
F V	0.95	-1%	0.95	0%	0.94	-1%	1%	1%
G	0.96		0.95		0.94			
G V	0.94	-2%	0.95	-1%	0.93	-2%	1%	1%
H	1.02		1.01		1.00			
H V	1.00	-2%	0.99	-2%	0.98	-2%	2%	2%
I	1.03		1.03		1.01			
I V	1.01	-2%	1.02	-1%	1.00	-2%	2%	2%
J	0.92		0.93		0.90			
J V	0.90	-1%	0.94	0%	0.89	-1%	2%	2%
K	1.04		1.05		1.00			
K V	1.03	-1%	1.04	-1%	0.99	-2%	2%	3%
L	1.09		1.10		1.06			
L V	1.07	-2%	1.08	-2%	1.05	-1%	2%	3%
N	0.93		0.92		0.91			
N V	0.92	-1%	0.92	0%	0.89	-2%	2%	2%

Cont.

Table 3. Continued

	Optical density without filter						L*	
	Damp heat aging				Light		Damp heat aging	light
	60°C		90°C		30°C		60°C	30°C
	DO	Variance	DO	Variance	DO	Variance	Variance	Variance
O	1.01		1.00		1.00			
O V	0.99	-1%	0.98	-2%	0.96	-3%	1%	2%
P	0.90		0.91		0.90			
P V	0.89	-1%	0.91	-1%	0.89	-1%	1%	2%

A: before ageing sample. A V: after ageing sample. DO: optical density average.

printing required hard abrasive conditions. The results were not reproducible with laboratory equipment. The inks could not be classified this way.

Damp heat aging. For aging at 60°C, L* values are rather stable, and black printing does not fade (Table 3). The small variance does not induce very substantial ΔE^* . There is not any color alteration after aging under damp heat. These results are confirmed by the low densitometric variance (which is never more than 3% during aging at 60°C) and in even harder conditions, such as 90°C. For each ink, pH is measured on flat areas that are cut up and ground together. The averages are calculated based on 3 measurements (Table 4). The pH is constant after aging and the pH of the non-printed permanent paper is about 9. This could be explained by the fact that ink is only 2% of the printed sheet weight; this quantity is not high enough to influence printing pH. Furthermore, offset inks are not acid.

Light aging. The density variance before and after light aging (Table 3) remains lower than the variance due to the precision of the apparatus (± 0.02). This demonstrates the preservation of the visual qualities of black printing. This result is confirmed with the study of L*, which practically never changes (less than 3%).

Conclusion. Artificial damp heat aging did not alter the color or density of the 15 black printings. The pH of samples was not modified. The study of penetration on the paper allowed some inks to be preliminarily classified. Black offset inks for current sheet-machines are compatible with permanent paper. Moreover, their use guarantees the permanency of such printed records.

Table 4. pH before and after damp heat accelerated aging

Scale	pH			Moy	pH V			Moy	Δ pH
A	9.11	9.09	9.04	9.08	9.16	9.14	8.83	9.04	-0.0
B	9.02	9.05	9.15	9.07	9.09	8.89	9.25	9.08	+0.0
C	9.27	9.33	9.32	9.31	9.34	9.33	9.29	9.32	+0.0
D	9.37	9.33	9.31	9.34	9.38	9.42	9.40	9.40	+0.1
E	8.93	9.00	8.95	8.96	9.02	9.07	9.04	9.04	+0.1
F	9.20	9.15	9.12	9.16	9.23	9.21	9.20	9.21	+0.1
G	9.18	9.22	9.32	9.24	9.21	9.23	9.19	9.21	-0.0
H	9.20	9.22	9.26	9.23	9.29	9.28	9.25	9.27	+0.0
I	8.98	9.04	9.05	9.02	9.18	9.21	9.18	9.19	+0.2
J	8.93	8.91	8.93	8.92	8.92	9.00	9.02	8.98	+0.1
K	9.08	9.05	9.13	9.09	9.20	9.16	9.12	9.16	+0.1
L	9.12	9.16	9.13	9.13	9.26	9.27	9.26	9.26	+0.1
N	9.27	9.31	9.28	9.29	9.35	9.36	9.34	9.35	+0.1
O	9.18	9.17	9.17	9.17	9.23	9.20	9.21	9.21	+0.0
P	9.10	9.11	9.14	9.12	9.08	9.13	9.07	9.09	-0.0

pH: pH of printings before aging. pH V: pH of printings after aging. Moy: pH measurement average. Δ pH: pH average difference of printings.

Colored inks

Damp heat aging. Without a filter, the optical density, after hard aging at 90°C, shows only slight variance (Table 5). Gaps are increased for measurements with complementary filters, in particular for magenta and yellow, which reach a loss of 10% (Table 6). But that remains less important than the modification of the paper itself.

Color investigations with the microspectrophotometer were not carried out because of the slight optical density variance.

Light aging. Extensive kinetic research allowed us to follow the changes in printing color. This is illustrated by densitometric graphs under complementary filters (Fig. 2) and color difference graphs L^* a^* b^* (Fig. 3-5). Optical density measurements with red filter show slight variance for cyan printings (less than 5% after 350 h). The variance in a^* and b^* values during the aging remains very low: this shows the stability of this tint. Optical density measurements with green filter show that, for magenta printings, the color fades slightly, about 15%. Kinetic study denotes a continuous color fading. There is only one more stable ink, with a fading less than 5% (T ink, Red P 28710, Sun Chemical). A detailed examination of color graphs shows that

Table 5. Optical density without filter before and after damp heat accelerated aging

	DO	DO-Perm	(V-T)
Cyan			
M	0.62	0.56	
M V	0.66	0.58	0.02
Q	0.69	0.63	
Q V	0.73	0.64	0.01
Magenta			
R	0.61	0.55	
R V	0.61	0.53	-0.02
S	0.59	0.53	
S V	0.60	0.51	-0.02
T	0.59	0.53	
T V	0.60	0.51	-0.01
U	0.60	0.54	
U V	0.62	0.54	0.00
Yellow			
V	0.08	0.02	
V V	0.12	0.04	0.02
W	0.08	0.02	
W V	0.16	0.07	0.05
X	0.09	0.03	
X V	0.14	0.06	0.03
Y	0.09	0.03	
Y V	0.13	0.05	0.02
Z	0.09	0.03	
Z V	0.13	0.05	0.02
permanent paper	0.06		
permanent paper V	0.09		

fading is essentially represented by the lightness component L^* and not by the tint a^* and b^* . For yellow printings, optical density variance under a blue filter is more pronounced: it could reach 70% in the Y ink, but is about 40%. The examination with the microspectrophotometer shows that the modification of the color is mainly due to a^* b^* variance, which approaches 0. This color change corresponds with a saturation decrease and not with a tint variance. The L^* component changes less (yellow lightness is already very high, around 90). One special ink (which does not correspond with the exact tint required

A
V1: 885m, n93
N93.14.3

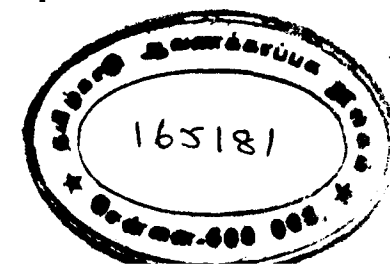


Table 6. Optical density with filter before and after damp heat accelerated aging

	DO	DO-Perm	(V-T)	(V-T)/T
Cyan				
× 100 with red filter				
M	0.92	0.87		
M V	0.89	0.83	-0.04	-5%
Q	1.00	0.95		
Q V	0.97	0.91	-0.04	-4%
Perm	0.05			
Perm V	0.06			
Magenta				
× 100 with green filter				
R	1.03	0.97		
R V	1.00	0.91	-0.07	-7%
S	1.00	0.94		
S V	0.96	0.87	-0.06	-7%
T	1.05	0.99		
T V	1.01	0.92	-0.07	-7%
U	1.02	0.96		
U V	0.99	0.90	-0.06	-6%
Perm	0.06			
Perm V	0.09			
Yellow				
× 100 with blue filter				
V	0.74	0.65		
V V	0.76	0.59	-0.06	-9%
W	1.02	0.93		
W V	0.99	0.82	-0.10	-11%
X	0.95	0.86		
X V	0.93	0.76	-0.10	-11%
Y	0.82	0.73		
Y V	0.85	0.68	-0.05	-7%
Z	0.95	0.86		
Z V	0.94	0.77	-0.10	-11%
permanent paper	0.09			
permanent paper V	0.17			

for the yellow of the four-color process) keeps fading less than 5% (W ink, yellow G 28105, Sun Chemical).

If we examine the lightfastness given by the manufacturers (Annex 3), the strongest printing corresponds with inks that have the highest index: 8 for

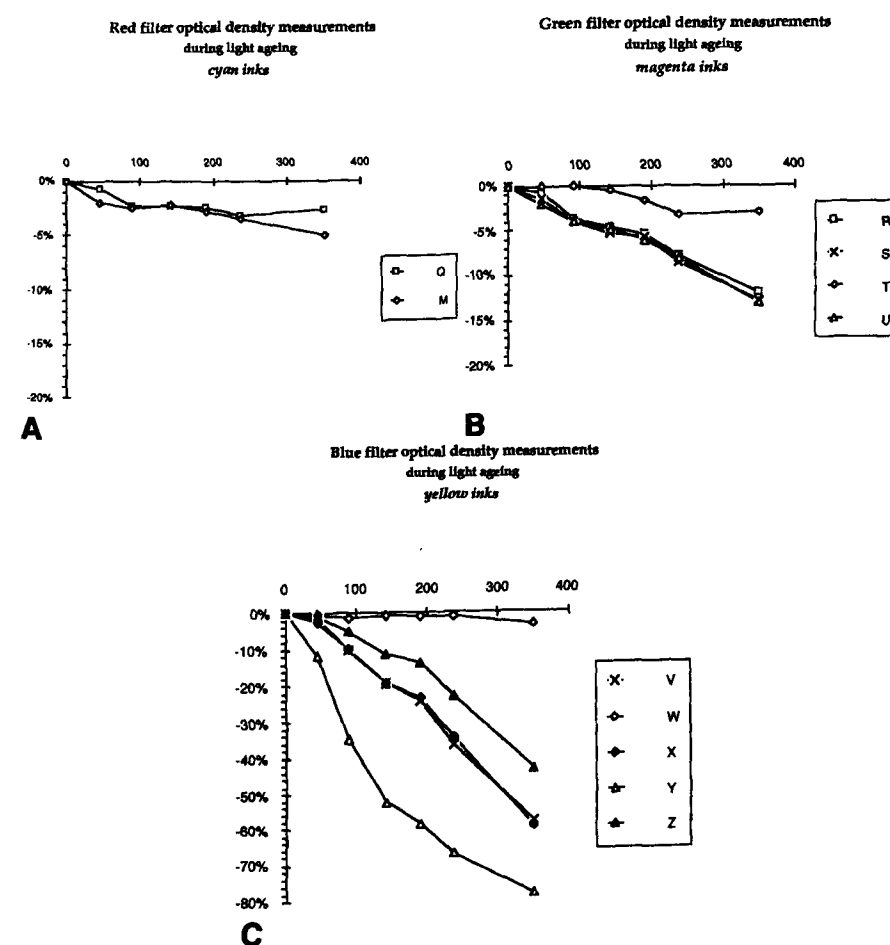


Fig. 2. Optical density measurements during light aging. A. Red filter for cyan inks. B. Green filter for magenta inks. C. Blue filter for yellow inks.

cyan inks, 6 for magenta ink, 7 for special yellow ink and 5-6 for the other best yellow inks. Variation from one ink to the others is principally due to the pigments (Annex 9).

Conclusion. The tested cyan printings are very stable; the magenta ones and especially yellow ones are less stable.

So the choice of inks directly affects the permanence of colored records on permanent paper. Moist heat aging is not very active but the light exposure can change the visual properties, by selective fading of some magenta ones, but especially most yellow ones.

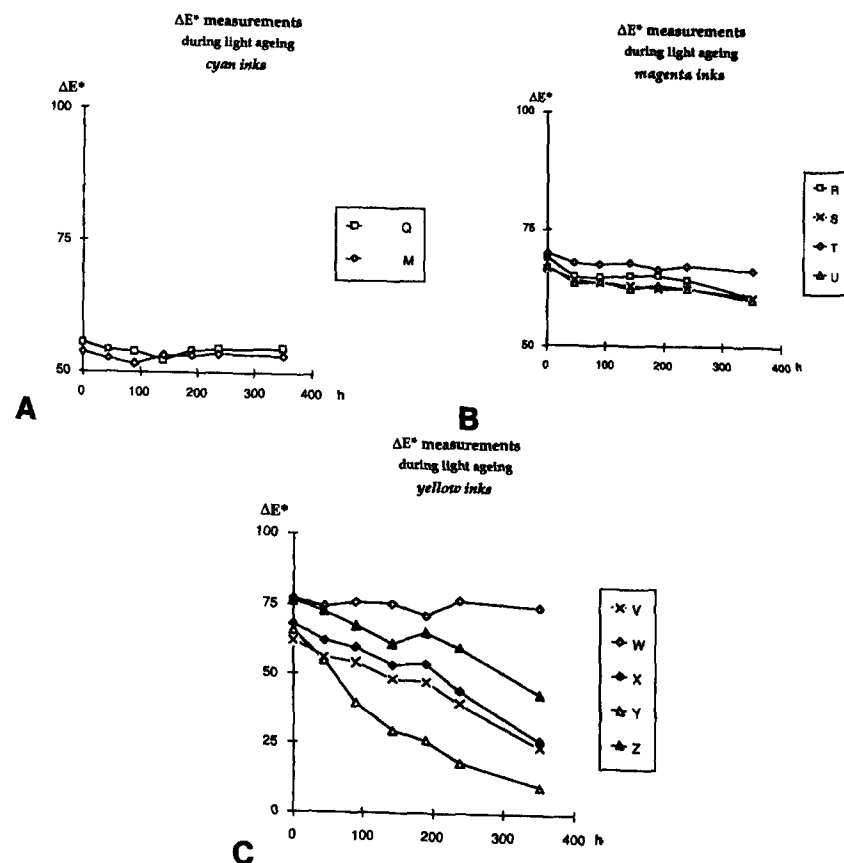


Fig. 3. ΔE^* measurement during light aging. A. Cyan. B. Magenta. C. Yellow inks.

CONCLUSION

The Centre National des Lettres du Ministère de la Culture et de l'Education Nationale is one of the rare authorities that is interested in the conservation of printed records. The problem of permanent paper has been resolved in France for many years, but the compatibility and the stability of printing inks on permanent paper has not been researched.

That is why we performed this study. A bibliography limited our research to the main book-printing process in France: offset. The inks were selected in close collaboration with the main manufacturers in France. A preliminary study directed us to select inks that seemed compatible with permanent paper. The whole four-color process scale was examined: 15 black inks and 11 colored inks (2 cyan, 4 magenta and 5 yellow).

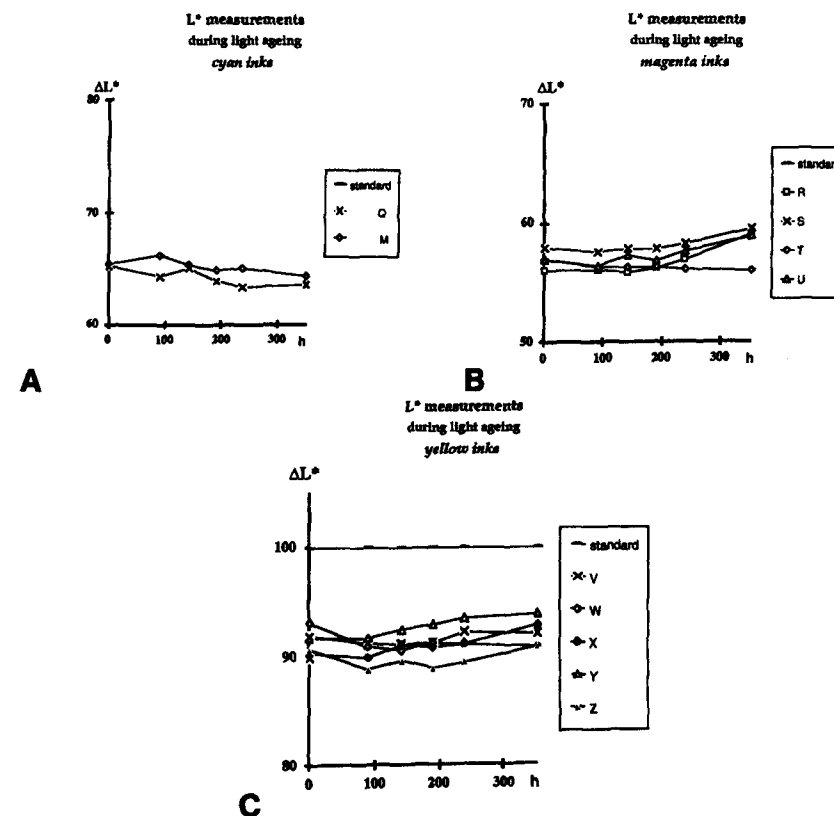


Fig. 4. L^* measurements during light aging. A. Cyan. B. Magenta. C. Yellow inks.

Samples composed with various forms used in the offset process were printed with a current sheet-machine in the EFPIG workshop. They were subjected to two kinds of accelerated aging: moist heat and light. Previous modifications were noticed by measuring optical density, color and pH.

Black printings keep their chemical and visual qualities before and after artificial aging. The stability of offset-printed texts is thus certain if permanent paper is used.

Quantification trials of printing qualities were realized according to two technologies: abrasion results were not conclusive, but measurements suggested a black ink classification according to penetration in paper.

The tested colored printings showed more disparity. They are not really affected by the damp heat aging; light exposure changes magenta and particularly yellow printings. Fading, which could reach total discoloration in some yellow printings, is then observed on most printings.

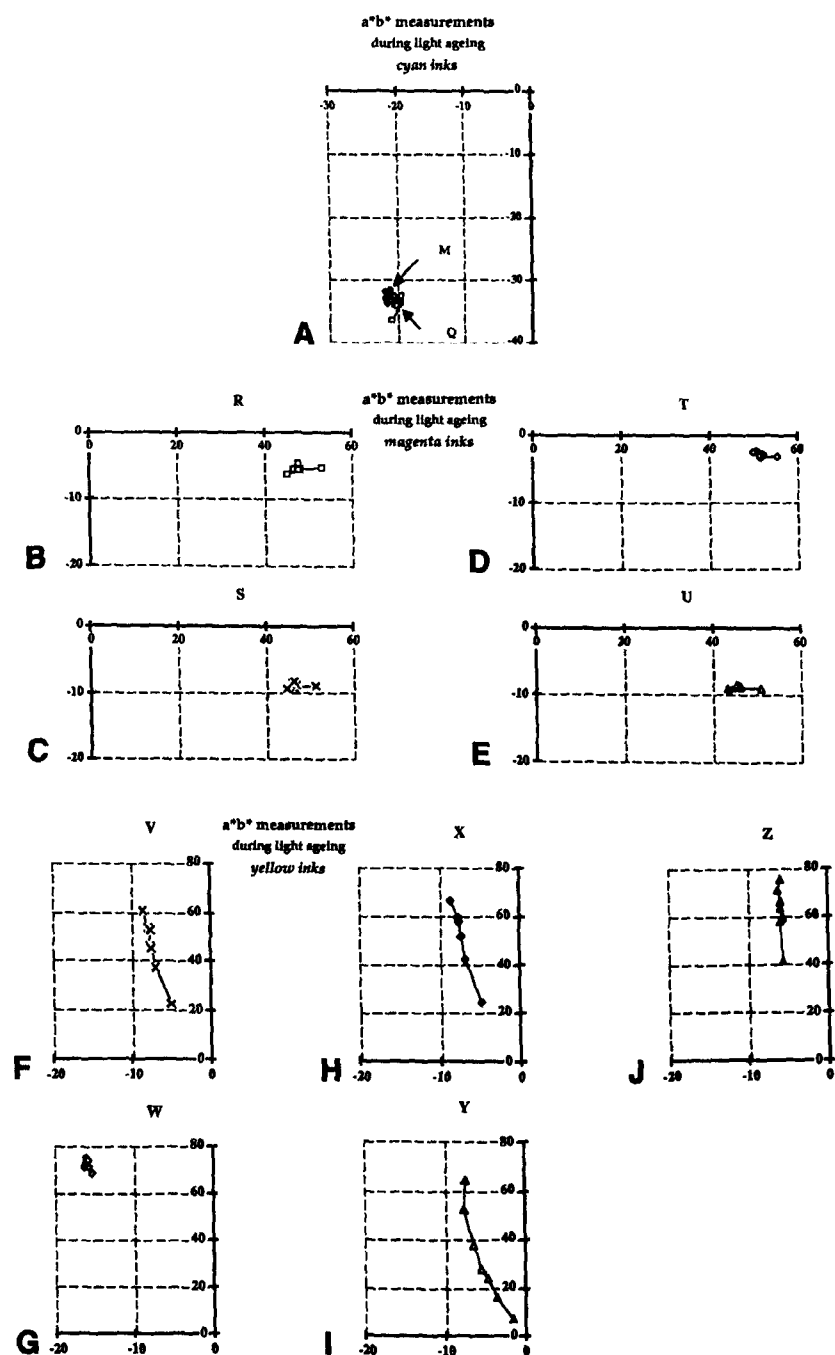


Fig. 5. a^*b^* measurements. A. Cyan. B-E. Magenta. F-J. Yellow inks.

A careful choice of inks could improve the printing stability: printers should select the strongest and most lightfast ones (index > 5).

This study allows us to prove the compatibility of permanent paper with current printing inks used in a sheet-offset press. It specifies the perpetuity of such printed texts and warns against the instability of colored documents, which are light-sensitive.

A careful choice of conservation methods for printed documents and the graphic materials used during their production remains absolutely necessary for the transmission of our cultural heritage to the future generation.

ACKNOWLEDGEMENTS

We thank Mr. Michel Richard, investigator of these works, which have been carried out with the financial assistance of CNL. We also thank Mr. Baudin, manager of the printing section of the Ecole Française de Papeterie de Grenoble, for his active participation. He allowed us to use his laboratory and introduced us to printing ink specialists. We also express our thanks to the manufacturers who helped us in our research and, more particularly, those among them who let us into their plants and informed us on the making of inks and how they are controlled: Mr. Sirost (Research and Development Manager, Lorilleux), Mr. Mathelin (General Manager, France-Couleur Sun Chemical) and Mrs. Moreau (Technical Manager, France-Couleur Sun Chemical).

SUMMARIES

The Stability of Printing Inks

After an introduction to printing inks, their origin, their composition and their use, a report is given on exhaustive testing of the stability of black and colored printing inks, also when they are stressed by light and by damp heat accelerated aging. The general result confirms the observation of book conservators: the permanence of printed books is governed by the permanence of their paper. This is true for inks used for offset printing, the most widely used printing process. Printing inks are quite stable: much more stable than colored documents.

Stabilité des encres d'imprimerie

Après une introduction sur les encres d'imprimerie, leur origine, leur composition et leur utilisation, on décrit les tests complets réalisés pour évaluer la stabilité des encres d'imprimerie noires et de couleur soumises à des vieillissements artificiels à la lumière et à la chaleur humide. Les encres noires sont très stables, ce qui n'est pas le cas pour les encres de couleur, dont certaines pâlissent à la lumière.

Die Dauerhaftigkeit von Druckfarben

Nach einer Einleitung in die Druckfarben, ihre Herkunft, Zusammensetzung und ihren Gebrauch wird über ausführliche Versuche zur Dauerhaftigkeit von Druckerschwärze und Druckfarben berichtet. Die Untersuchungsmethode war die Belastung durch Licht und die Lagerung bei stark erhöhter Temperatur und Feuchtigkeit (beschleunigte Alterung). Das allgemeine Ergebnis bestätigt die Erfahrung von Buchrestauratoren: gedruckte Bücher sind so dauerhaft wie ihr Papier. Dies trifft gerade auch für den Offsetdruck zu, das heute meistgebrauchte Druckverfahren. Druckfarben sind generell sehr stabil: viel stabiler als farbige Dokumente.

REFERENCES

1. Archambeaud, P. & Fain, J.F.: *Encres d'imprimerie, noir et couleur, fabrication et emploi*. Paris: INIAG, 1965.
2. Audin, M.: *Histoire de l'imprimerie, radioscopie d'une ère: de Gutenberg à l'informatique*. Paris: Picard, 1972.
3. Fontaine, M.: *Encres d'imprimerie*. In: *Chimie des peintures, vernis et pigments*, vol. 2. Paris: Dunod, 1956: 248.
4. Martin, G.: *Les matières premières de l'imprimerie, papiers et encres*. Paris: INIAG, 1979 (Collection Espace).
5. Vanderhoff, J.W.: *Introduction to printing inks*. In: Division of Organic Coatings and Plastics Chemistry Paper. 17th Meeting of the American Chemical Society 37,2 (1977): 161-6. Washington, DC: American Chemical Society, 1977.
6. Chiodi, R.: *L'impression des papiers: description des procédés d'impression*. Grenoble: EFP/FCV document n°313. 1976.
7. Martin, G.: *L'imprimerie*. Paris: PUF, 1990.
8. Durchon, P.: *Photogravure et impression offset*. Paris: édition du moniteur, 1987.
9. Sirost, J.C.: *Offset: le rôle de la plaque*. In: *L'imprimerie Nouvelle* 40 (January/February 1986): 23-8.
10. Eldred, N.R., & Scarlett, T.: *What the printer should know about ink*. Pittsburgh: Graphic Arts Technical Foundation, 1990.
11. Flick, E. W.: *Printing ink formulations*. Park Ridge: Noyes Publications, 1985.
12. Leach, R. H.: *The printing ink manuel*. London: Van Nostrand Reinhold, 1988.
13. Cahierre, L.: *Encyclopédie des industries graphiques*. Volume 2. *Les encres*. 2nd edn. Paris: Compagnie Française d'Editions, 1979.
14. Grandou, P., & Pastour, P.: *Encres d'imprimerie*. In: *Peintures et Vernis*. Paris: Hermann, 1969: 301.
15. Racelis, F.: *The composition of inks*. Conservation Administration News 29 (April 1987): 6-10-13.
16. Sirost, J.C.: *L'encre, la fabrication*. Caractère 227 (January 1988).
17. Wolfe, H.J.: *Printing and litho inks*. New York: Mac Nair-Dorland, 1967.
18. Young, L.C. & Fiopfric, B.S.: *Materials in printing process*. London: Focal Press, 1973.
19. Patton, T.C.: *Pigmentation of commercial printing inks*. Pigment handbook 2 (1972).
20. Sirost, J.C.: *L'encre d'imprimerie, vers la recherche d'un compromis*. Caractère 218 (September 1987): 55-9.
21. Sirost, J.C.: *L'encre, les pigments*. Caractère 223 (November 1987): 57-60.
22. Carbonnier, M.: *L'encre d'imprimerie: composition de l'encre destinée au procédés d'impression offset feuilles*. France Echange Graphique International 45 (1988): 4-7.
23. *Pigment black for printing inks*. Degussa technical bulletin pigments. no. 10. Frankfurt am Main: Degussa, September 1990.
24. *Carbon blacks for coatings and printing inks - a survey*. Degussa technical bulletin pigments. no. 15. Frankfurt am Main: Degussa, February 1986.
25. Carlick, D.J.: *Physical-chemical similarities among typical printing ink resins*. American Ink Maker 62, 12 (1984): 27-30, 32, 34, 36, 38, 40, 42, 46, 48, 53, 54, 58, 62.
26. Sirost, J.C.: *L'encre, son véhicule*. Caractère 225 (December 1987): 56-60.
27. Sirost, J.C.: *L'encre, sa composition*. Caractère 219 (October 1987): 69-72.
28. Sirost, J.C.: *La maîtrise de l'impression offset*. La France Graphique 14 (1987): 10.
29. Sirost, J.C.: *Le transfert offset*. In: *L'imprimerie Nouvelle* 31 (July/August 1984): 25-33.
30. Chiodi, R.: *Les tests d'imprimabilité*. Grenoble: EFP/FCV document n°334. 1976.
31. *Des Encres d'impression*. Communication Imprimée 26 (1989): 17.
32. Grandou, P., & Pastour, P.: *Contrôle*. In: *Peintures et vernis*. London: Van Nostrand Reinhold, 1969: 375-416.
33. Martin, G.: *Considérations sur l'étude des relations encre-papier à l'aide des presses miniatures*. L'imprimerie Nouvelle June 1961, pp. 3-9, July-August 1961, pp. 3-11, September 1961, pp. 3-16, October 1961, pp. 3-22, November 1961, pp. 3-16, December 1961, pp. 5-16, February 1962, pp. 15-26, March 1962, pp. 3-23.
34. Ray, C.T.: *Printing ink*. In: *Painting testing manual*. Philadelphia: G.G.S. Ward, 1972: 490.
35. Edelman, E.: *La résistance des impressions aux agents physiques et chimiques*. Imprimerie Nouvelle (February 1962): 17.

ANNEX 1. PRINTING PROCESSES

Source: Eldred & Scarlett¹⁰

Process	Method	Examples
Planographic	Printing from flat surface	Lithography Collotype
Intaglio	Printing from recessed surface	Rotogravure Steel die
Relief	Printing from raised surface	Letterpress Flexography
Stencil	Ink forced through a stencil	Screen printing Mimeograph
Electrostatic	Image carried electrostatically	Xerography Electrofax Laser printing
Ink jet	Ink droplets	Ink jet printing

ANNEX 2. STANDARDIZED TESTS

Lightfastness

The sample is exposed under sunlight or, for an accelerated test, under a xenon lamp until an alteration defined on a gray scale (no. 3). Then we note the degree

of etalon tone corresponding with the alteration of the sample. We obtain numbers from 1, for the minimum resistance, to 8, for the maximum resistance.

Alkaline resistance

The samples are pressed by the printed side against the filter paper previously plunged in a caustic soda solution, with the possibility to use another base. Then we note printing alterations and also the running of water on the filter paper. In offset the soda concentration is 25% in weight. In fact, the pressure between two glass plates is 1 kg for 10 min; then the filter paper is dried under air flow and observed; the sample is neutralized by successive washing with water and then dried for 30 min at 50°C.

Solvent resistance

The sample is plunged into selected solvents for a defined time. Then we note the coloration of solvents and the changing of the printing tint. The usual standard is a 5-min immersion followed by 10 min at 50°C drying. For the resistance to alcohol, ethanol is generally used.

ANNEX 3. LIST OF SAMPLES

The figures in brackets [] are the lightfastness values given by the manufacturers.

Black inks				
A	Lorilleux	Black TS 250	réf	774 128
B	Lorilleux	Contrast Pantone Black	réf	774 589
C	Lorilleux	Black Matemil	réf	195 481
D	SICPA	Black - varnishable	réf	12 500
E	SICPA	Black Carton	réf	8 803
F	SICPA	Black - varnishable	réf	3 150
G	Grant	Black	réf	660
H	Grant	Black	réf	9 093
I	Grant	Black	réf	505
J	Sun Chemical	Univit Black neutral P	réf	S 28 900
K	Sun Chemical	Univit Black Primaire	réf	S 2 890
L	Sun Chemical	Univit Black Primaire	réf	S 2 880
N	Brancher	Black Vignette	réf	34 000
O	Brancher	Black Edition	réf	22 300
P	BASF	Polyking	réf	85

Cyan inks				
M	Sun Chemical	Univit Blue Primaire	réf	B 282 [8]
Q	Lorilleux	Major Blue Primaire GEU	réf	8 125 [8]
Magenta inks				
R	Lorilleux	Major Red Intense	réf	8 135 [4]
S	Lorilleux	Major Red Primaire GEU	réf	8 127 [4-5]
T	Sun Chemical	Red	réf	P 28 710 [6]
U	Sun Chemical	Univit Red Primaire	réf	P 28 110 [5]
Yellow inks				
V	Sun Chemical	Univit Yellow Primaire	réf	G 2800 [5]
W	Sun Chemical	Yellow	réf	G 28 105 [7]
X	Sun Chemical	Yellow	réf	G 28 110 [6]
Y	Lorilleux	Major Yellow Primaire	réf	8 126 [3]
Z	Lorilleux	Major Yellow Solide	réf	8 154 [5]

ANNEX 4. VISCOSITY AND RIGIDITY MEASUREMENTS

Time (in seconds) for a 10-cm distance is measured with different overweights (600–200 g) and reported on an abacus. The intersection of the obtained line and the abscissa gives the rigidity (dynes/cm); whereas the parallel passing by 0 allows extrapolation of the viscosity value (poise) and a comparison to typical lines of known viscosity.

The whole apparatus is made in unoxidizable steel and is maintained at 25°C; the detection of time of falls is realized with a stopwatch started by photoelectric cells.

ANNEX 5. TACK MEASUREMENTS

The equipment is formed with 3 thermostat cylinders at 32°C; two in synthetic rubber: one is moving parallel to its axis (to achieve homogeneous inking); the other one is moving perpendicular to its axis (for the measurement); the third one is metal and contacts the two others. It permits the distribution of the ink and the tack measurement.

The protocol consists in putting 0.5 ml of ink on the rubber inker cylinder with a large syringe; the three cylinders are put in rotation for 30 s at 50 m/s, then for 30s at 100 m/s. The recorder measures the movement of the mobile cylinder that is perpendicular to its axis; this movement corresponds with the strength necessary to separate the ink film between the two cylinders. As the tack changes during the measurement, we only keep the first recording value.

ANNEX 6. PRINTABILITY TESTS

The equipment has three inking cylinders, two in metal and one in rubber, with a spanner covered with synthetic rubber. The protocol consists in depositing a

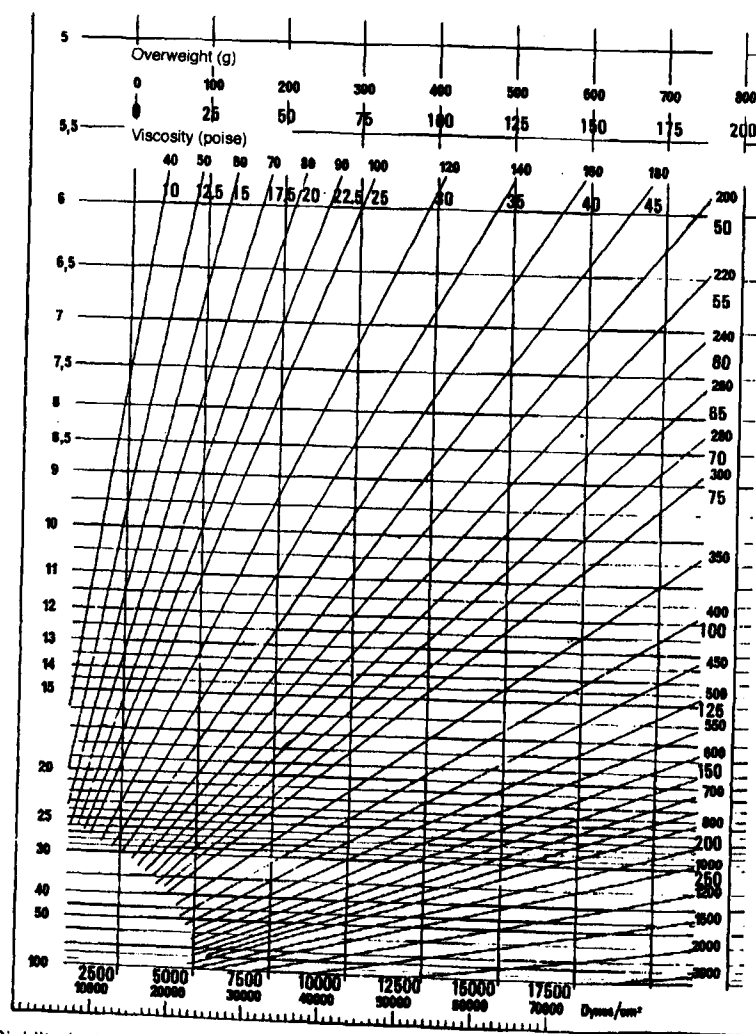


Fig. 6. Rigidity (poise) and viscosity (dynes/cm²) measurements (see Annex 4)

quantity of ink on the inking system and achieving homogenization, after about 30 s; the spanner is then put in close contact with the inker and weighed after 30 s of rotation.

The printing is then realized by having constant speed and pressure on a strip of paper. Under the inked spanner, we can obtain uniform printings of known surface. A new weighing of after printing spanner permits the quantity of the ink deposited to be calculated and then the ink weight for 1 m². In our case we used permanent paper strips and we tried to obtain inking values of about 1.5 g/m² with a range from 1.45 to 1.55 g/m².

ANNEX 7. MACKLES

The freshly printed strip is covered with a blank strip, and pushed under a non-inked spanner after 1, 3 and 5 min. We obtain dirt on the blank strip: if the ink dries slowly, the mackles are more important.

Strips printed on the Prüfbau can be used for optical measurements. France-Couleur laboratory has a reflectance spectrometer.

ANNEX 8. COLORIMETRIC CALCULATIONS

Colorimetric calculations are made on averages according to the following formulas:

$$\begin{aligned} L^* &= 116 (Y/Y_n)^{1/3} - 16 & X &= (0.785 RX) = 0.167 RZ \\ a^* &= 500 [(X/X_n)^{1/3} - (Z/Z_n)^{1/3}] & Y &= RY \\ b^* &= 200 [(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}] & Z &= 1.008 RZ \end{aligned}$$

RX, RY and RZ are the averages of measured values. X_n, Y_n and Z_n are etalon values of white nominal stimulus of the equipment. L* corresponds with the brightness (100 for white etalon). a* and b* correspond with the tint and the saturation (0 for white etalon).

The total color difference could be quantified by:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$$

ANNEX 9. COLOR INDEX

Different pigments are usually classified by the Color Index (CI). For the current four-color process offset inks, the following is chosen:

Yellow

Diarylides yellows based on the diazotated 3,3' dichlorobenzidine, followed by a linkage with two acetoacetarylde molecules.

CI Pigment Yellows 12 – acetoacetanilide – Diarylide AAA

CI Pigment Yellows 13 – 2,4-acetoacetoxylidide – Diarylide AAMX

Magenta

CI Pigment Red 57: 1 – “Red Rubis lithol”: Ca salts coming from the linkage of paratoluidine metasulfonic with β-oxynaphtic compounds

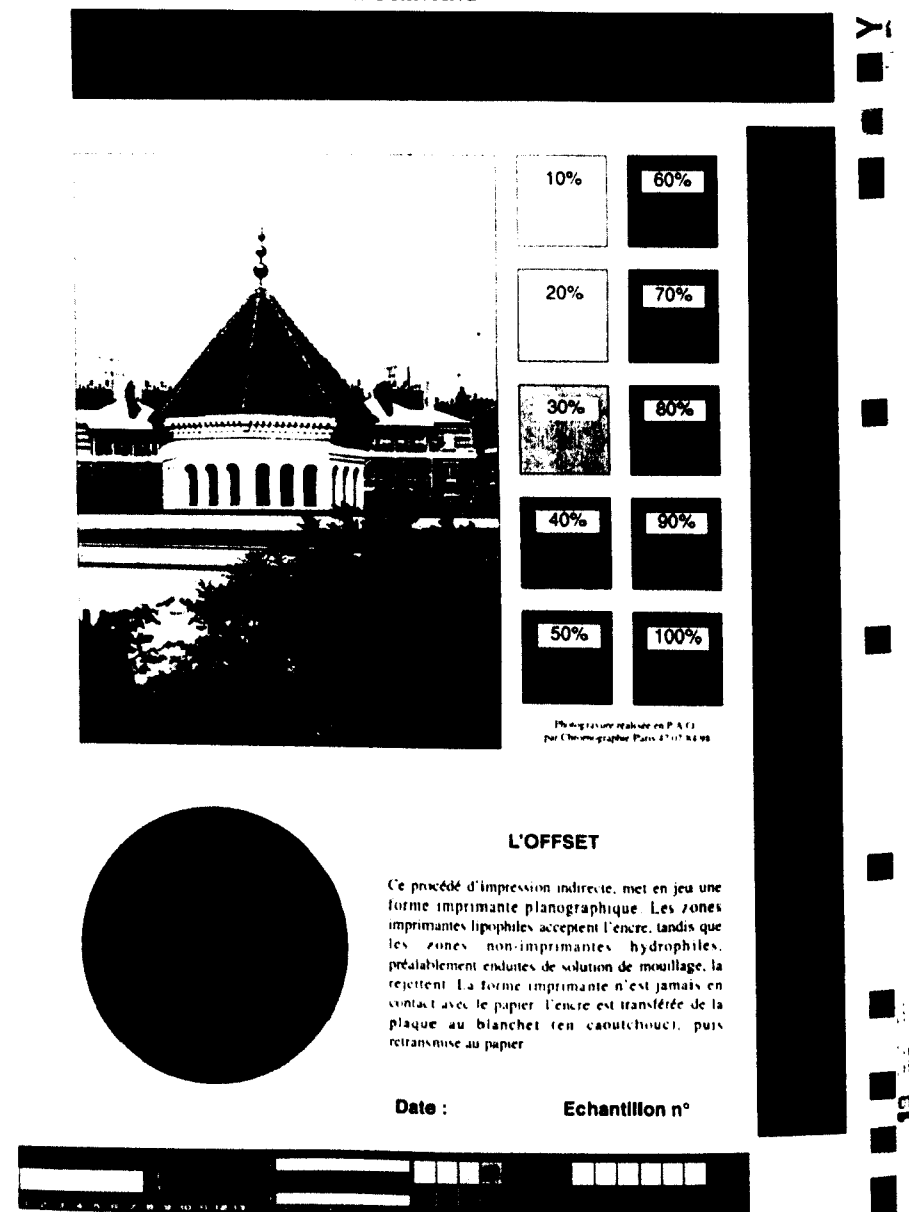
Cyan

CI pigment blue 15: 3 – blue phthalocyanine – β copper form

These pigments are used in offset because they are appropriate to the process

and because of their visual qualities. However, only the blue ones are known to be very lightfast. But red and yellow ones are less stable.

ANNEX 10. PATTERN USED FOR PRINTING



Martine Maraval
Association de la Recherche Scientifique
sur les Arts Graphiques
36 rue Geoffroy-Saint-Hilaire
F-75005 Paris, France

Françoise Flieder
Centre de Recherche sur la
Conservation des Documents Graphiques
36 rue Geoffroy-Saint-Hilaire
F-75005 Paris, France

A New Approach to Systematic Dry Cleaning with Technical Devices

by RICHARD MOROZ & EVA ROEVER

INTRODUCTION

There is no need to discuss the necessity of dry cleaning. However, in most workshops dry cleaning is carried out in the same way on nearly all objects. The traditional manual dry cleaning with erasers either in powder form or as solid gums is the most common technique to dry clean objects of art on paper.

This might well be sufficient for workshops that conserve objects of a less complex nature but does not satisfy the expectations from the work done in the Zentrale Restaurierungswerkstatt (ZRW). The ZRW-Haus Lüttinghof is a conservation centre within a regional governmental body in northwestern Germany. The task is advice on passive conservation in 200 local museums in the area and the conservation and restoration of their collections. The condition of these collections is often quite unmentionable. Many of the museums rely on the work of volunteers to be able to survive, often retired schoolteachers or craftsmen without any knowledge of museum management.

Due to the described situation, the standards of lighting, climate and strong-room keeping often leave a lot to be desired. The condition of the objects sent to the conservation centre obviously reflect the conditions in the museums they come from.

The ZRW was opened in September 1991 to provide first-class conservation for the museums founded by the regional government. As the government had spent a large sum of money to equip the centre with all the latest conservation technologies, the expectations towards the quality of work were very high and the staff was very motivated to use the good working environment. A project

on systematic dry cleaning and the use of technical alternatives to manual dry cleaning was started because the results from conventional dry cleaning were not considered good enough.

A more systematic approach to dry cleaning, especially of objects of art on paper, should also help in planning and carrying out conservation treatment more efficiently. An average of three conservators in each of the workshops in the centre work for 200 museums, so major capacity problems are unavoidable. Being economical and efficient is therefore also very important.

All types of prints, drawings, books, parchment, vellum and leather objects require conservation treatment at the centre. When objects are received for conservation they are categorized according to the structure of the paper, printing or drawing media and condition. The individual level and type of soiling and dust on the surface has to be checked prior to planning the conservation. Dust, soot, insect excrement and coarse particles of mud are types of dirt that have to be removed by means of dry cleaning. They differ considerably in their components and adhesion to the paper surface. Dirt can, for example, consist of coarse or fine, dry, moist or greasy particles.

The objective of dry cleaning has to be defined to choose a suitable technique. Should the dirt be removed as far as possible, and what does that mean in the individual case? The aspect of preservation is mainly relevant. How far does the dirt harm the object and impair its condition? Damaging dirt should always be removed as far as possible without affecting the surface of the paper.

However, objects with high aesthetic demands often require more cleaning than would be necessary under purely conservational aspects. In the paper conservation department of the ZRW, the treatment of objects of art on paper forms most of the work. Relief and intaglio prints, lithographies, pencil, charcoal and chalk drawings, watercolours, gouaches, pastels but also oil on paper and cartridge are typical objects. Books, pamphlets and documents are less common but have to be treated from time to time as well.

Obviously some printing and drawing media present more problems during conservation than others. For example, cleaning the verso of a charcoal drawing can lead to considerable loss of particles on the recto. Paper surfaces also vary from rough and coarse to smooth or from open and soft to dense and firm. Dry cleaning of rough surfaces can damage them; dirt and eraser particles are difficult to remove. Surfaces with a heavy texture cannot be cleaned effectively with eraser gums. Dry cleaning powder, how-

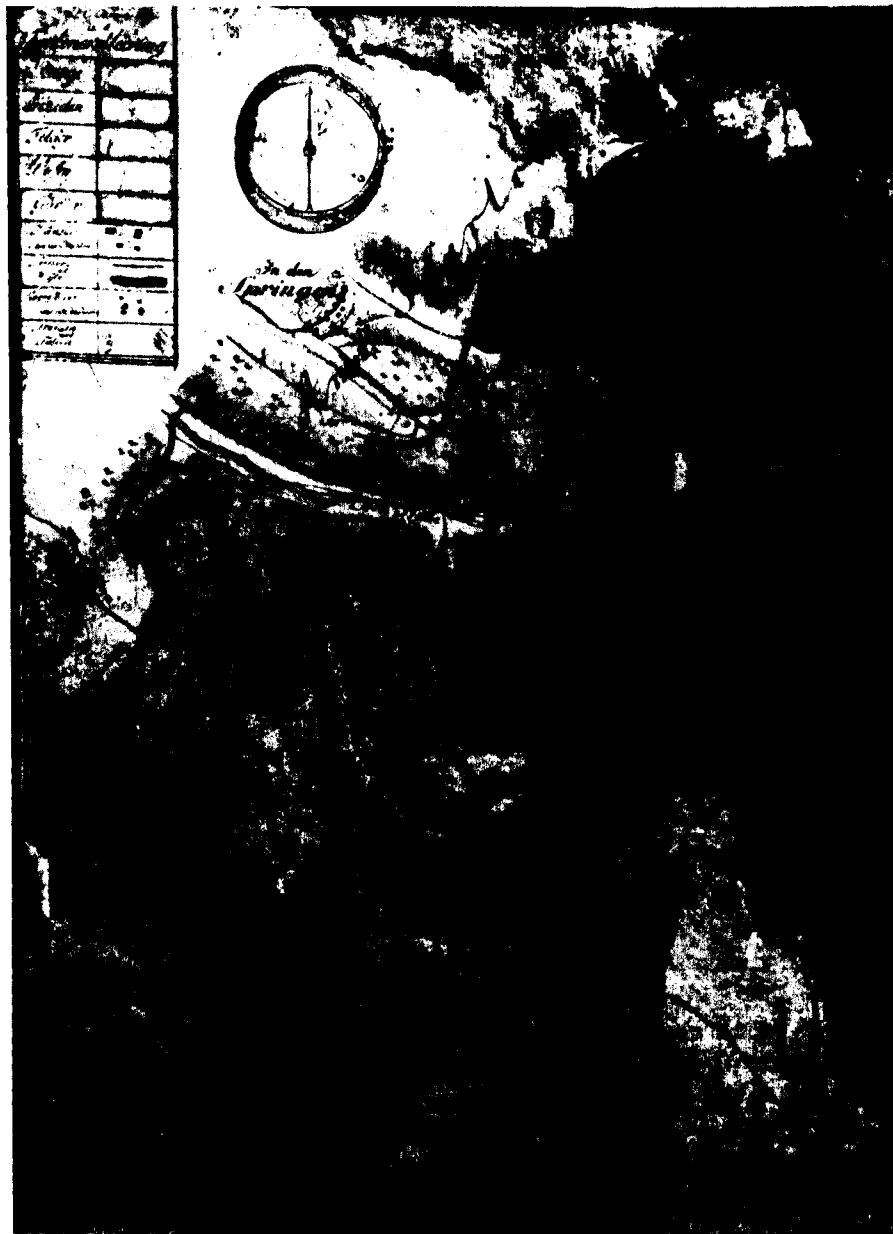


Fig. 1. Hand-drawn map with heavy soot soiling showing the three steps of the dry-cleaning process

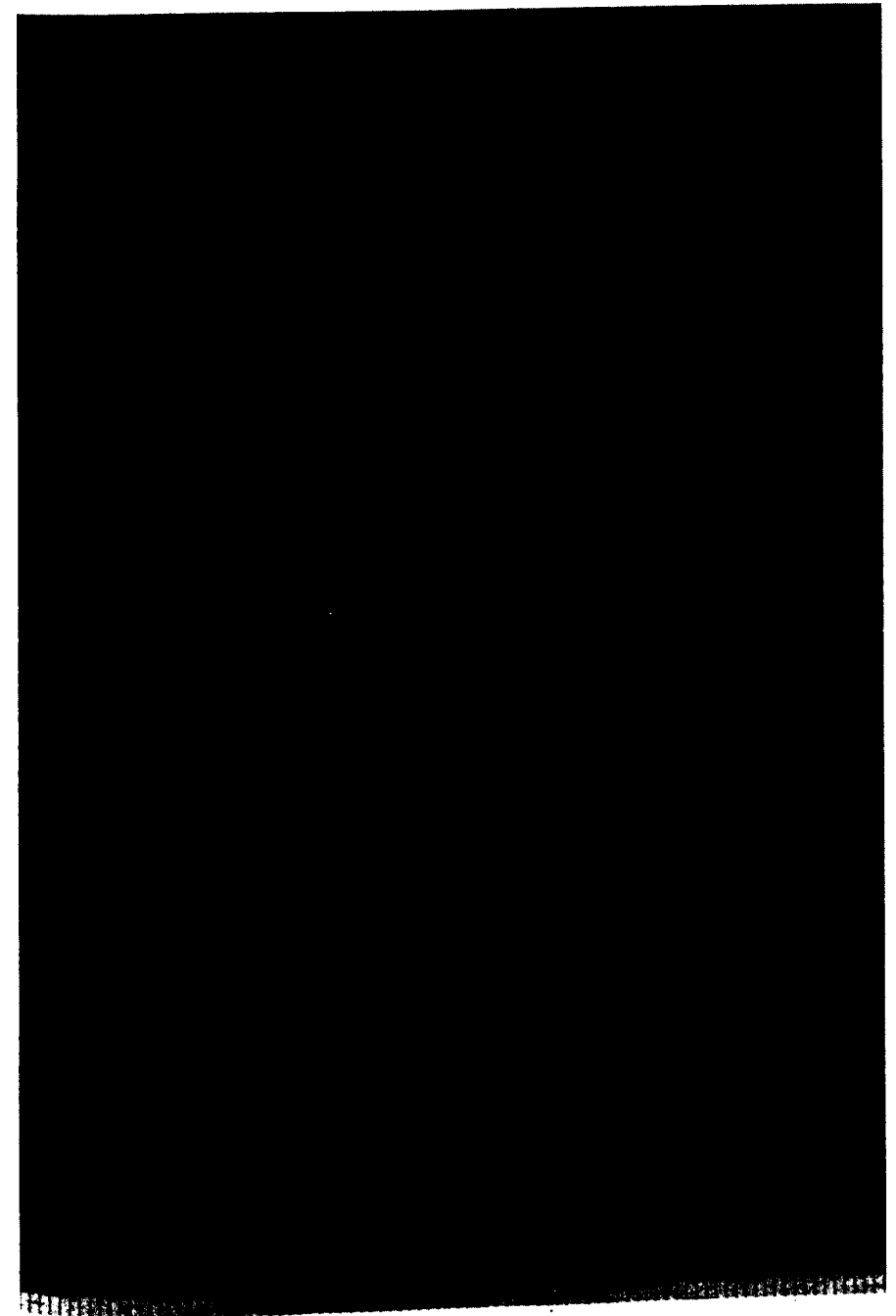


Fig. 2. "Panorama of Lemgo", ink and gouache drawing before dry cleaning, test patch cleaned manually

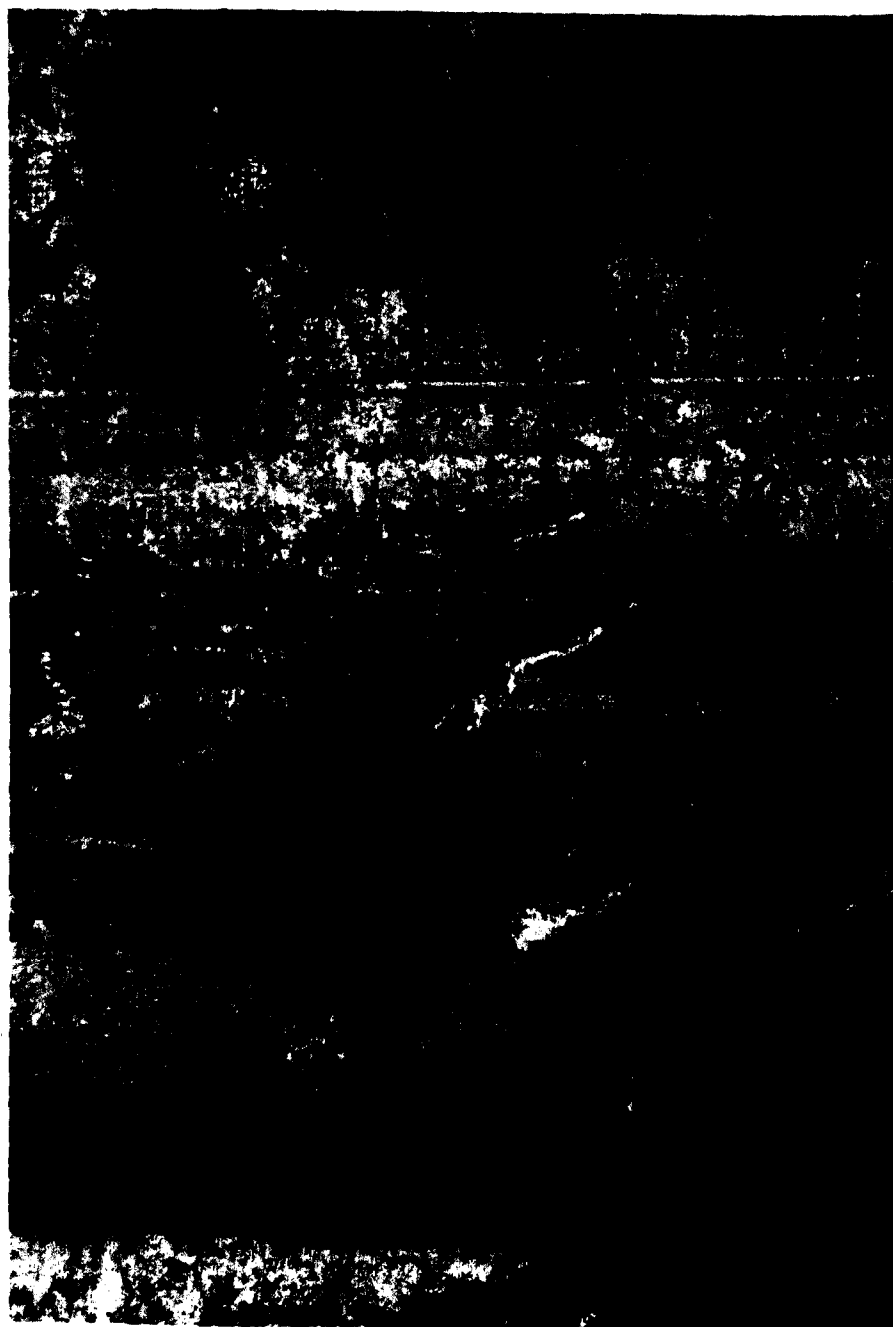


Fig. 3. "Panorama of Lemgo" dry cleaned, partially with electric eraser, partially manually; better results of electric eraser cleaning showing clearly

ever, does not give the same cleaning results when the same level of pressure is applied.

OBJECTS TREATED DURING TESTS

The aim of the tests was to find ways of dealing with the dry cleaning of the described objects by means of new techniques and the introduction of mechanical devices. The materials chosen for the tests were all recommended by the conservation literature or by colleagues. The electric eraser devices and the micro sand blaster were chosen from conservation equipment catalogues. To represent the variety of objects coming up for conservation, the following examples were chosen for the test:

- The eighteenth-century engraving "Fürstin von Gallitzin" was a typical intaglio print with very thick printing ink. The print was moderately dusty.
- Wood cuts by the German artist Wilhelm Morgner printed on thin Japanese paper were the next examples. The pictures were dusty with bad tears that were coarsely mended.
- Example number three was a sixteenth-century mass and prayer book with wood cut printing. Due to mould damage the paper was very open and soft. Because of heavy use the pages were very dirty and torn.

The most complex problems were found on the "Panorama of the town of Lemgo", an ink and gouache drawing. The picture consists of four types of paper that were pasted down onto very coarse linen. The paper surfaces varied from very open to very dense. Due to the linen the surface had a heavy texture. The paper was extremely dusty and dirty because of unprotected hanging in the museum over a long period of time. Large parts of the drawing had severe tears that were cemented and retouched with wallpaint.

Another typical example for an object damaged through inadequate conditions was a map drawn with ink and watercolours. Due to storage next to the coal stock in the museum cellar, the surface was covered in soot. Because of severe water damage, the map was very deformed and parts of the surface were abraded.

To test the sand-blasting machine, an intaglio printed map was chosen that was stuck onto coarse linen, which gave the surface its texture. Other objects dry cleaned during the test were a pencil drawing on brittle tracing paper, a red chalk drawing, a family tree on vellum drawn with ink, gouache and gold leaf.

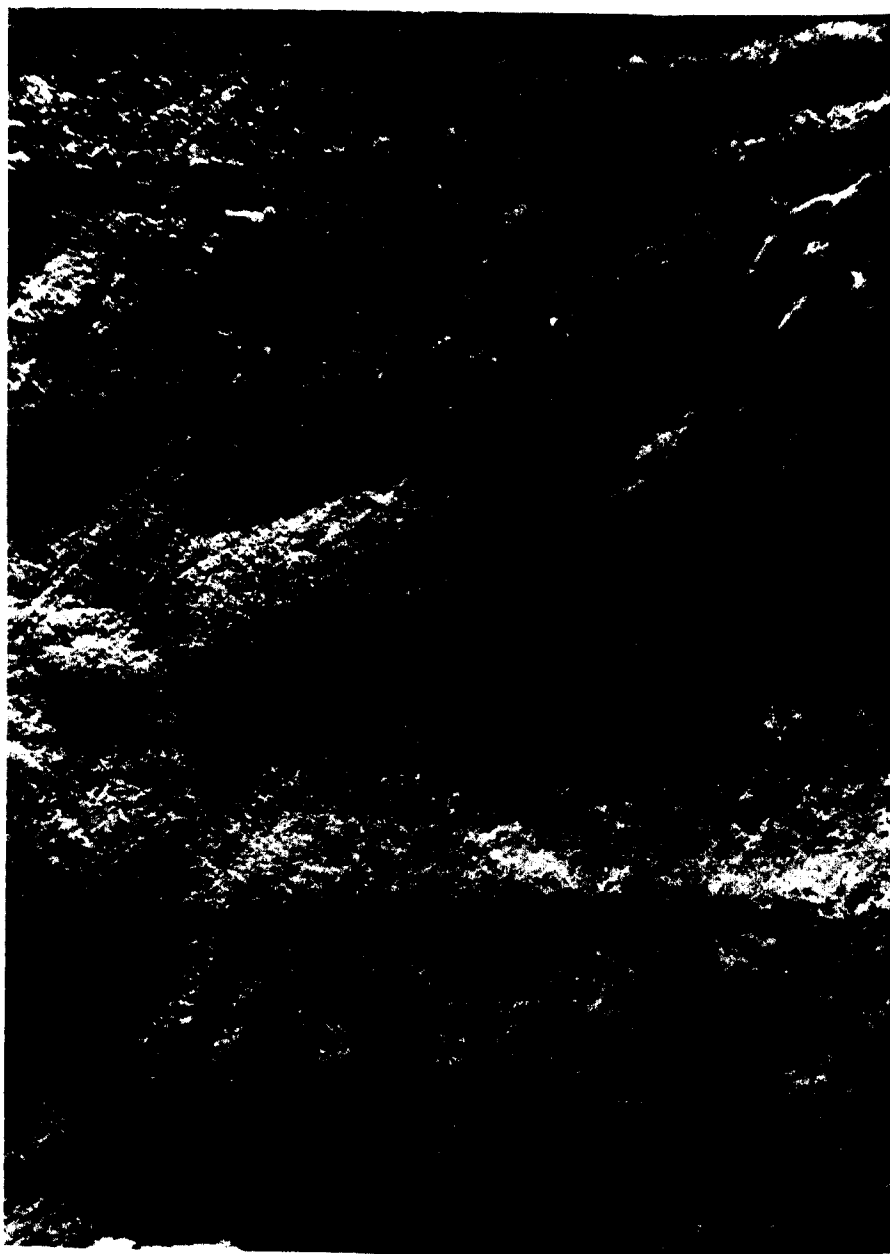


Fig. 4. Intaglio printed map, upper half cleaned with micro sand blaster

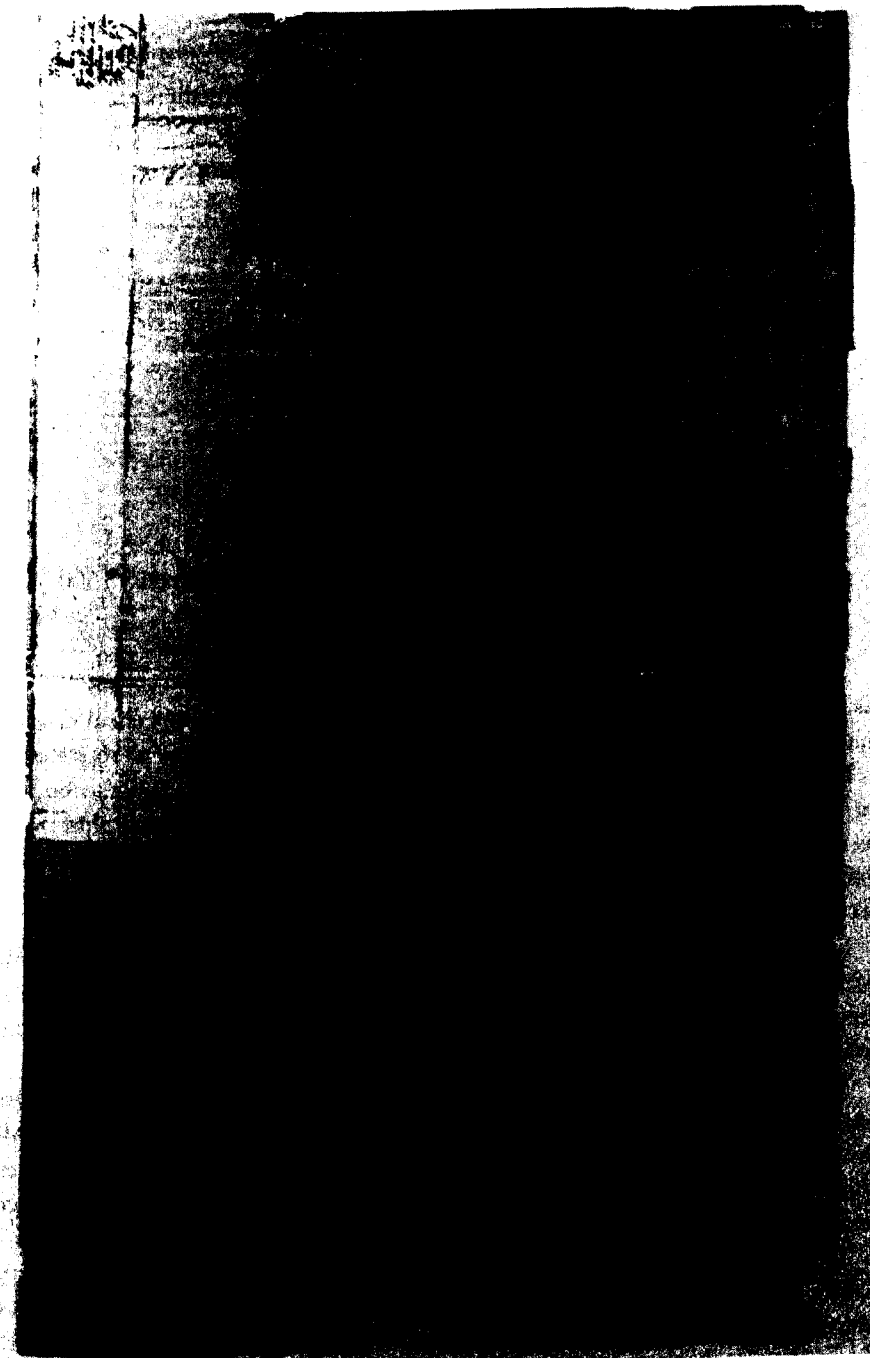


Fig. 5. Hand-drawn map with foil backing partially removed, from left to right: dry cleaned with electric eraser, foil removed, foil still in place

MATERIALS AND TECHNICAL DEVICES

The following materials and technical devices were used in the tests:

1. Dry cleaning powders
 - Draft Clean Powder, latex composition
 - blasting powder, bachelite and antistatic agent
2. Block erasers
 - TK-Vinyl 7081 N, vinyl composition
 - Supra 340, latex composition
3. Eraser mines
 - Pentel Clic Eraser, vinyl composition (Pentel)
 - Ecobra 3925, vinyl composition
 - Peel-off Magic Rub, vinyl composition (Magic Rub)
4. Erasing machines
 - Ecobra 4901, electric eraser, battery-driven, 2500 rpm (Ecobra S)
 - Ecobra 3901, electric eraser with built-in 12-V power pack, 1500 rpm (Ecobra)
 - Mikromat 100, micro sandblaster

As an alternative to manual dry cleaning with block erasers, electrical erasing machines are used in the ZRW. Two types of erasing machines were tested.

Device number one is a very light and slim machine that is built to be run on batteries or accumulators. An electricity cable and two switches were recently fitted to increase the utility. The first switch has three positions for different numbers of revolutions. The direction in which the eraser mine revolves can be changed with the other switch.

Electric eraser number two is considerably heavier and larger. It is built with a stronger motor and fitted with an electricity cable. The strong motor gives this machine a very uniform performance, as it can compensate the braking effect of pressing the mine onto the surface.

The eraser pens and mines can all be used in the devices described; the paper wrapping around the "Magic Rub" pens can be peeled off easily. All the mines tested are vinyl products with sanding additives. The latex mines commercially available are mostly too coarse and hard for the use on paper and therefore have not been tested.

The third machine tested was the micro sand blaster. As it is already very commonly used in metal conservation, it can also be used to work on paper objects. It was used where other dry cleaning techniques could not reach all parts of the surface, as it is the case on strongly textured surfaces.

Table 1. Development of heat in paper during the use of electric erasers measured with a digital brass sensor thermometer. The time was taken with a stopwatch and the data were registered photographically

Time (seconds)	Temperature (°C)			
	Ecobra Pentel	Ecobra S Pentel	Ecobra Magic Rub	Ecobra S Magic Rub
0	22.2	23.2	22.4	22.1
1.38		24.2		
2.28			24.6	
2.57		24.6		
4.18				23.2
4.30		26.7		
4.46	23.3	23.3		
5.26			29.1	
5.84				24.2
6.42		27.9		
6.86	25.2	25.2		
7.30			32	
7.82				26
8.80		30.7		
9.78	28.2	28.2		
10.22			34.1	
10.37				28.3
11.30		31.8		
11.40	31.4	31.4		
13.22				31.6
13.40		33.1		
13.46	34.7	34.7		
15.06			37	
15.57		33.1		
15.86	37.5	37.5		
16.00				34.1
16.50			38.6	
17.02	38.8	38.8		
17.57		33.6		
17.76				35.2
19.10			40.3	
19.36		35		
21.10				35.3
23.20		37.3		
23.22				35.5
30.37				36.2

Table 2. Development of heat directly in the brass sensor

Time (seconds)	Temperature (°C)			
	Ecobra Pentel	Ecobra S Pentel	Ecobra Magic Rub	Ecobra S Magic Rub
0	22.7	22.5	21.6	22.4
1.79		23.4		
2.16				33.3
2.82	25.1			
3.64			25.4	
4.00				30.8
4.73		26.9		
4.90			28.8	
5.00	34.9			
5.54				35.8
5.73		30.1		
6.73		32.2		
7.06			33.5	
7.34				40.7
7.40	41.2			
7.75		35		
8.32	45.1			
8.75		36.7		
8.92			36.4	
9.00				44.3
9.75		39.1		
10.51		31.4		
10.70				47.6
10.94			40.2	
11.32	50			
11.53		42.6		
12.34				51.7
12.59		45.3		
12.60			43.9	
13.20	53.4			
13.84				
14.66			46.7	
15.00	55.2			
16.48			48.7	
17.00	55.6			
21.75		47.6		
23.75		49.4		
24.73		50.6		
26.19		51.8		
27.31		52.9		
28.51		53.2		

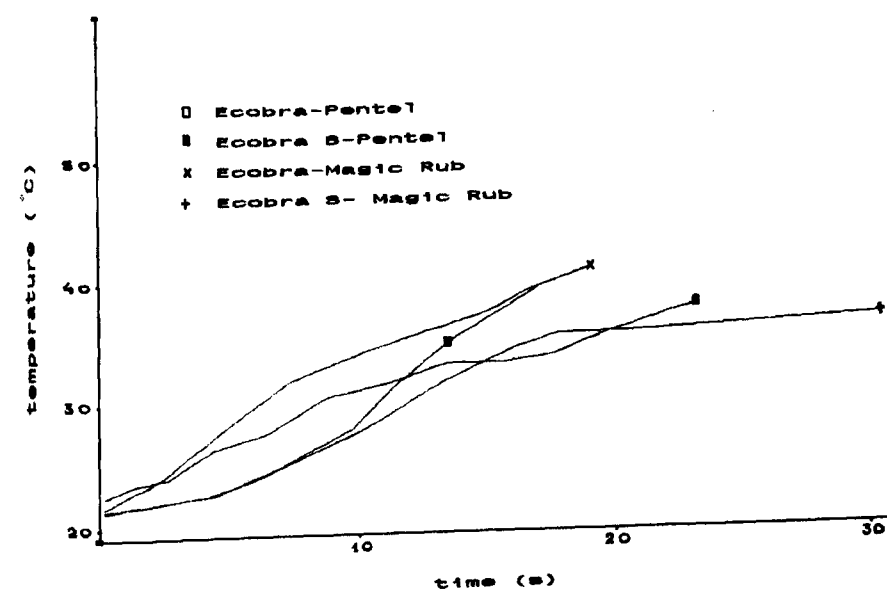


Fig. 6. Development of heat in the paper (see Table 1). After an initial period of 3-6 s, the curves show a quick rise

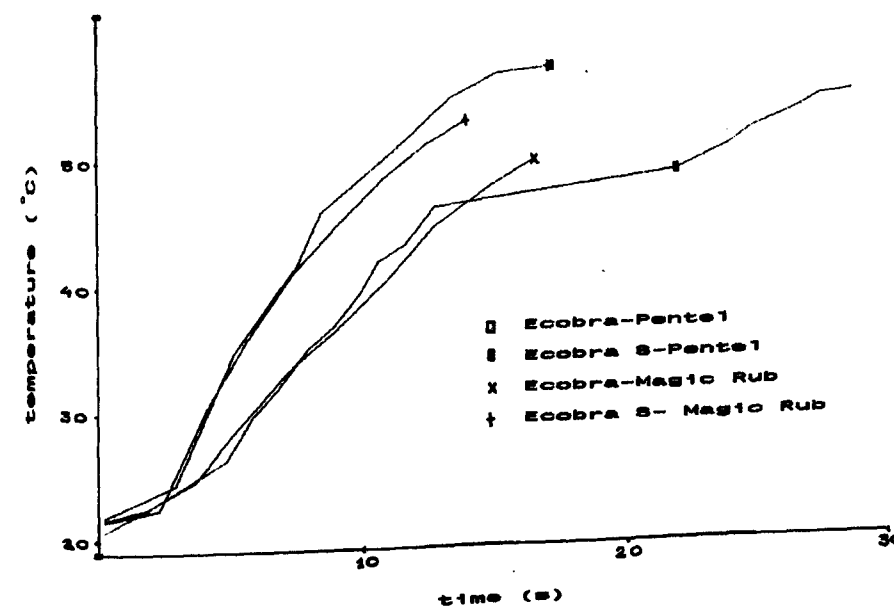


Fig. 7. Development of heat in the brass sensor

Block eraser or dry cleaning powder do not give satisfying results so this otherwise unconventional method was considered. The air pressure level used was one bar. The rubber powder used in the micro sander was very fine bachelite powder. Latex powder was considered but proved too coarse and blocked the nozzle. The vinyl powder tends to clod due to static charges so an antistatic agent should be added. The powder was tested in three grain sizes mixed with an antistatic agent.

The surfaces treated during the tests were analyzed using the KAPS SOM 62 stereomicroscope with $\times 25$ magnification.

DRY-CLEANING PROCEDURES

Once erasing materials and techniques have been chosen, the dry cleaning procedure has to be planned. It is often not sufficient to follow the rule of cleaning the verso before cleaning the recto and to work in one direction only on each side. Tears and edges around missing areas should be left out and treated separately. A sheet of paper should be inserted between the sides of a tear so each side can be thoroughly cleaned. Old infills in missing areas should therefore be removed before dry cleaning. If impossible, the dry cleaning has to be continued after the wet treatment. In many cases another attempt to dry clean objects after wet treatment is worth considering, as dirt that was previously deeper in the paper structure becomes more loose and can sometimes be lifted off.

Dry cleaning objects of art on paper often means taking into consideration the aesthetic aspect. A typical example is the dry cleaning of the "Lemgo Panorama". The dry cleaning procedure was to be carried out in several steps. Each step was the cleaning of a certain part of the drawing; in this case the picture had five parts that were to be cleaned separately. This method of dry cleaning was defined as partial gradual dry cleaning. In practical terms this means that, due to the aesthetic meaning of the picture, it is divided into several parts that are cleaned to a different degree. As usual, the procedure is started with the very soft latex powder. Working mainly from top to bottom the dry cleaning started on the sky, followed by the mountains, the town area, the banderol and the coat of arms.

The next material used was vinyl block eraser, starting on the sky again. Sky, mountains and the banderol were cleaned this way. The town area and coat of arms were just very lightly cleaned because of brittle pigment layers. When the drawing was cleaned to this degree, all loose surface dirt seemed to be removed so the dry cleaning was considered finished.

Several weeks later the two erasing machines were acquired and tested. A

part on the drawing was cleaned with device number two and the "Magic Rub" mine with very good results. After this test patch, the sky, mountains and landscape were dry cleaned with the machine. Considerable dirt was lifted by the treatment. It was not clear, however, whether the results were due to the new device or the fact that previously strongly adhered dirt had loosened over a period of time. To find out about this, more objects were dry cleaned with electric erasers. On all objects some parts were fully cleaned in one operation. On other parts the dry cleaning was split into several operations with at least two weeks between each step. Particularly suitable for this test was the hand-drawn map with heavy soot soiling.

DISCUSSION

As expected, the materials tested were suitable for use on paper, but there are large differences in how effective the materials and technical devices can be. It is evident that if the paper is strong enough to be cleaned with the electric erasers, the results are more even and more thorough than with manual dry cleaning. The differences between the two devices tested lie in their construction.

Machine number one is small and of very light weight. It is easy to handle, also over longer periods of time. The battery charge lasts for about 30 minutes, which led to a large demand for batteries and accumulators if it is used on larger surfaces. The cable fitted during the test was a valuable addition, as were the two switches. Different revolution levels are required to suit the individual surface and the revolution direction is equally important, for example, if overlapping edges are to be cleaned without inflicting damage.

Electric eraser number two is fitted with a motor strong enough to keep the number of revolutions per minute at a constant level even if more pressure is applied. This is very useful for work on heavily soiled objects.

The tests showed that each of the different mines is most effective in combination with a certain electric eraser. The light device number two is now used mostly with the very fine and soft Pentel and Ecobra mines. The eraser number two is used with the Magic Rub mines for heavier cleaning on less fragile surfaces. The dry cleaning carried out with the electric erasers was carefully examined and proved to be less stressful for the surface and results in more even and more thorough removal of dirt particles. The revolving movement of the mine does not damage the fibre structure if used appropriately and does not produce great heat in the paper.

In many cases the use of the electric devices also considerably reduces the time needed to complete the work.

The use of the micro sand blaster has brought very good results on the printed map with heavy texture. The fine, soft sanding powder does not damage the paper if used at low pressure. It does, however, get well into the depth of the texture and clean the surface very evenly. This method is particularly useful for larger collections of printed maps as it is also much less time consuming than manual dry cleaning. The micro sander should only be used on paper with a very dense and well sized structure.

CONCLUSION

1. Most of the thorough dry cleaning is now done by electric erasers. The quality is far better than with the same time spent on manual dry cleaning, as far as could be observed with the stereomicroscope.
2. Much consideration is also given to the planning of the dry cleaning. If possible, the different steps are carried out with at least a two-week break between them to allow the dirt to loosen. This makes the next step easier; sometimes a softer eraser can be chosen than had previously been thought.
3. The technique of partial gradual dry cleaning is used on objects with important aesthetic value that might not become so obvious if all parts were cleaned to the same degree. This is mainly relevant for objects of art on paper, which form the largest part of the objects in the department.
4. During conservation treatment, objects change both in their chemical and physical properties and their aesthetic requirements. Obviously analysis has to take into account both aspects. This paper is the first step in researching this subject and so far the emphasis was on the aesthetic requirements of the objects. Future analysis can include both chemical and aesthetic tests.

LIST OF SUPPLIERS

Draft Clean Powder, Archival Aids, United Kingdom
Bacelite Powder, Fa. Schlick, Metelen, Germany
TK Vinyl 7081 N, Peel-off Magic Rub, Faber Castell, Stein/Nürnberg, Germany
Supra 340, Fa. Läuffer, Burgdorf/Hannover, Germany
Clic Eraser, Pentel Co., Ltd, Japan
Ecobra 3925 and electric erasers 3901, 4901 (Speedy), Fa. Ecobra, Nürnberg, Germany
Ama-digit ad 31th, thermometer, Amarell Electronic, Kreuzwertheim, Germany

Mikromat 100, Micro Sand Blaster, Fa. Joisten & Kettenbaum, Germany
KAPS SOM 62, Fa. Kaps, ABlar, Germany

SUMMARIES

A New Approach to Systematic Dry Cleaning with Technical Devices

Dry cleaning is one of the most common and at the same time most neglected tasks in paper conservation. In the recently opened conservation centre Haus Lüttinghof, a series of tests was carried out to establish new dry cleaning systems. A systematic approach to dry cleaning of objects of art on paper, defined as partial gradual dry cleaning, was developed. Another aim of the project was to find out whether electric erasers and micro sand blasters could have a wider use in paper conservation. The use of electric erasers and the micro sand blasters on suitable paper surfaces has proved to give more even and thorough dry cleaning results than manual dry cleaning with block erasers and dry cleaning powder.

Nouvelle approche du nettoyage à sec systématique accompagnée de conseils techniques

Le nettoyage à sec est une des tâches les plus communes et en même temps les plus négligées en restauration du papier. Dans le centre de conservation Haus Lüttinghof récemment ouvert, des tests ont été réalisés afin de mettre au point de nouveaux systèmes de nettoyage à sec. On a développé une approche systématique du nettoyage à sec des oeuvres d'art sur papier défini comme nettoyage à sec partiel et progressif. Un autre but du projet était d'établir si les gommes électriques et les micro-sableuses pourraient avoir une plus large application en restauration du papier. L'utilisation de gommes électriques et de micro-sableuses sur des surfaces de papier approprié a résulté en un nettoyage à sec plus uniforme et plus en profondeur qu'un nettoyage à sec manuel avec des gommes ou de la gomme en poudre.

Neue Erkenntnisse und technische Ratschläge zum trockenen Reinigen

Trockenes Reinigen ist eine der häufigsten und gleichzeitig eine der am meisten vernachlässigten Arbeiten der Papierrestaurierung. In dem neu eröffneten Zentrum »Haus Lüttinghof« wurde eine Testreihe durchgeführt, mit dem Ziel, neue Verfahren der trockenen Reinigung der Kunst auf Papier zu erarbeiten. Es wurde eine Systematik dieser Technik erstellt; sie läßt sich definieren als partiell-graduelles trockenes Reinigen. Ein anderes Ziel des Projektes war es festzustellen, ob elektrisch betriebene Radierer sowie Mikrosandgebläse in der Papierrestaurierung eingesetzt werden können. Es zeigte sich, daß mit diesen Geräten eine gleichmäßigere und durchgreifendere Reinigung erreicht werden kann als mit Radiergummi und Radierpulver.

Richard Moroz
Eva Roever
Westfälisches Museumsamt
Zentrale Restaurierungswerkstatt
Haus Lüttinghof
Lüttinghofallee 2
D-4650 Gelsenkirchen-Hassel
Germany

Medieval Painting on Parchment: Technique, Preservation and Restoration

by G. Z. BYKOVA

GREEK PARCHMENT AND THE BYZANTINE TECHNIQUE OF MINIATURE PAINTING

Medieval illuminated manuscripts on parchment can be divided conditionally into two groups based on their technique: western European and Byzantine. They have different methods of preparing the parchment as well as different paint techniques.

Byzantine parchment is characterized by a glossy and smooth surface. Greek parchment-makers polished it thoroughly to obtain such an effect. There is evidence that they had used egg white and flax-seed for this purpose. Byzantine miniatures, as well as Old Russian manuscript painting, incorporated a multi-layer icon painting technique. It nearly always consists of underpainting (*san-kir*) with a few subsequent layers in lighter shades, heightened with white. Paint layers are dense; this can be explained by the presence of a considerable quantity of binding agent in it (Fig. 1).

This complex-smooth parchment with a heavy paint layer is the main reason for the poor preservation of miniatures in Greek manuscripts. The principal character of damage in these miniatures is detachment of the paint layer from the support, accompanied by losses of paints. It should be noted that there is still a sufficient quantity of binding media in them.

The gold in Byzantine manuscripts is applied in leaf-form and is attached directly to the support with help of some strong glue. On most occasions it is well preserved. But sometimes when the gold leaf is fixed to a thin coloured preparation (usually it is red ochre), it may peel off because of lack of binding. In turn, pigments nearly always detach easily from the gold surface, especially on the outlines of images standing against a gold background.



Fig. 1. Text in black ink on the glossy surface of a Greek Manuscript (13th century)

OCCIDENTAL PARCHMENT AND TECHNIQUE OF WESTERN EUROPEAN MINIATURISTS

Absolutely different phenomena may be observed in the case of occidental parchment manuscripts. Parchment-makers of western Europe in the final stages of their work rubbed chalk or pumice into the parchment. They made the fibres of parchment friable, and the surface became velvety, soft and mat. The texture on both sides of the sheet has a practically similar appearance. As a result, occidental parchment is not liable to the deformations typical of Byzantine manuscripts: characteristic rolling of edges of leaves.

It is difficult to write or draw in ink or colours on velvety parchment; the outlines of letters are not even; ink colours only partly the fibres of parchment, which are slightly raised from the surface. In illuminations, thin outlines drawn in ink have a broken appearance, because ink dyes only convex part of the parchment (Fig. 2).

A typical feature of the Western manuscript illumination technique was colouring a preparatory drawing accompanied by graphic modelling of the details. The garments of outstanding characters, architecture and other details of composition could be coloured by the same pigment. The modelling of garments usually was reduced to graphic treatment of folds. Features of faces

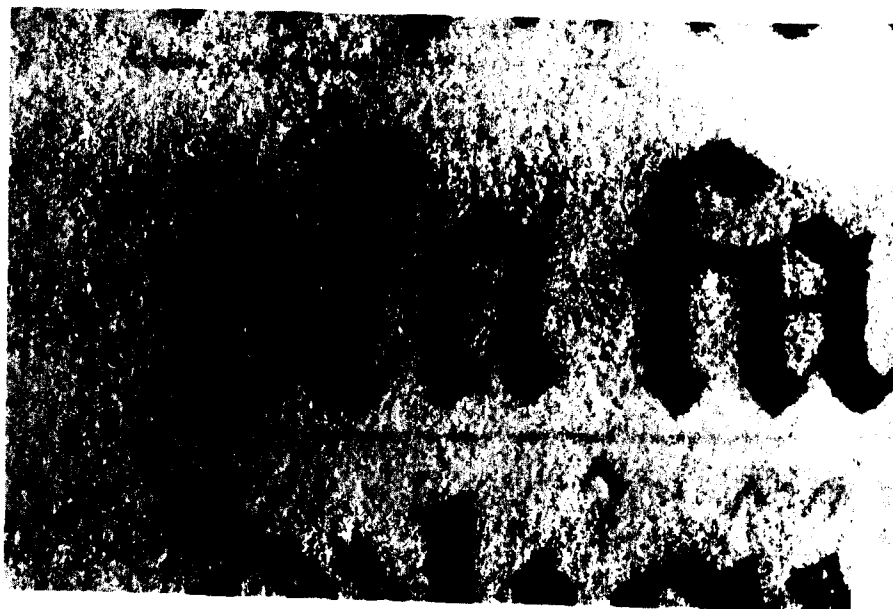


Fig. 2. Text in black ink on velvety texture of a French manuscript (15th century)

were outlined in ink or black pigment. But naked parts of the body and the face were coated with white lead, which formed a thick layer and often got damaged and easily detached from parchment. Sometimes the faces of characters were touched by watery red colour. So, in Western illumination it occurs that only faces, hands or some naked parts of bodies painted in white lead could be affected by destruction, and only these parts of miniatures may require necessary treatment in most cases.

A particular feature in the technique of occidental miniaturists is their method of gilding. Gold leaf was placed on a thick base composed of glue and chalk, sometimes coloured red, grey or black. This dense base was thoroughly polished, which was possible because of the considerable quantity of glue in it. That leads to a convex appearance of such details as nimbuses beside backgrounds. Sometimes this preparation for gilding gets destroyed because of its excessive thickness and lack of glue, whereas the golden leaf itself is stuck safely to the base.

So one may say that the technique of Western book illumination combines a very thin paint layer with a thick specially prepared base for gilding.

STATE OF PRESERVATION OF THE PAINT LAYER IN BYZANTINE MANUSCRIPTS

On the contrary, the gilding process in Byzantine miniatures was done directly on the parchment: numerous layers of pigments formed one dense layer that surpassed of course the thin colour film of western artists. Poor preservation of Byzantine miniatures and analogous to them of technique (such as Old Russian, Georgian, Balkan) can be explained not only by considerable density of paint layer but also by the degree of its cohesion with parchment.

Now let us observe the leaf of Greek parchment with painted miniature on it just before proceeding to start the conservation process (Fig. 3):

- First of all, one can see sections with losses of paint layer. In some cases a preparatory sketch could be distinguished. As a rule these sketches are well preserved, because they were executed with red organic pigment or diluted ink that was absorbed easily even by the polished surface of Byzantine parchment.
- Some parts of miniatures coloured by organic pigments can be noted by their relative good preservation.



Fig. 3. Miniature from a Byzantine manuscript (15th century) before conservation treatment

- Then we see a considerable number of areas destroyed with detached multi-layer painting and painted sections on golden surface.

PRINCIPLES OF CONSERVATION IN TREATING A DETACHED PAINT LAYER

What should one do?

1. There is no need to treat parchment which is revealed under losses of paint. Any binding material used in any concentration would provoke its deformation.

2. The fragments of preserved painting are examined thoroughly with the help of a microscope to ascertain the firmness of its adhesion to support and to reveal damaged sections that need treatment.

Our principle of restoration of medieval miniatures is minimal interference with the texture of the paint layer. Practically, on very rare occasions one may observe complete detachment of the paint layer. Great damages to pigments are connected with technical particularities and methods of artists as well as the conditions of storage. We consider that only local treatment of damaged fragments is necessary.

As we had seen, the paint layer of Byzantine miniatures is firm enough by itself and is not in need of extra binding material for mechanical stability. It is necessary only to fix detached fragments of the paint layer to parchment, using the right quantity of binding media just for this or that fragment. The problem is to find material with certain technical properties that would let binding matter flow easily under detached fragments of paints. For all that, treated and untreated parts should not differ in colour and no halos should be formed around them. Attempts to fix the detached fragments by applying binding material directly on the surface of painting cannot be successful, because it remains on the surface and can provoke more destruction.

ANALYSIS OF METHOD AND MATERIALS USED IN CONSERVING TEMPERA PAINTING ON DIFFERENT SUPPORTS

Analysis of all recent methods of fixing tempera painting on different supports (such as paper or cardboard) helped us to draw the conclusion that all of them are reduced to impregnation of the paint layer with diluted solutions of glues or resins. This method is favourable enough for paper support, as it gets additional sizing, making it (paper or cardboard) more solid mechanically. Coloured sketches or prints are easily impregnated together with the support, and only a slight change in hue appears. But it is impossible to apply a glue on a restricted unmoistened area, because it will immediately provoke darkening of

colours and the appearance of halos. So this method and materials could be successfully applied only to graphic works.

Mechanical transfer of this method for treatment of medieval painting on parchment is absolutely unjustified, because here we have different support, paint technique and character of damages.

Attempts were made to apply fish-glue for fixing the paint layer on parchment, but that had only provoked additional destruction. The molecular structure of animal glues (that is, fish-glue, parchment glue, gelatine) does not make it possible to use them locally, without heating, even in case of low concentration of their solutions. The surface tension of water does not make it possible to fix detached particles of pigment to the parchment: they rest on the surface of each drop of the solution. And moreover the particles can easily be turned upside down and be replaced. It could be possible to apply such a glue solution on the whole surface of the painting, but the colours will change considerably. And still it will be impossible to remove the surplus of glue from the surface, because animal glues are dissolved only in warm water and that will lead to deformation of parchment and additional losses of paint. The remains of glue on the surface of the paint layer will considerably provoke its shrinkage and more destruction.

In western European illuminations (13th–15th centuries) one can observe very often some details glazed with egg white or some kinds of gum. That is a well known effect, which was applied for instance by famous Russian artists of the beginning of the twentieth century (Golovin, Korovin), who often worked in tempera. Glazed parts turned out to be darker than the rest of painting and translucidity of glazing preserved the original colouring. In due course the glazed particles of paints sometimes start to peel off. Some of them have raised edges and that may lead to losses.

As early as in 1961, chemists and restorers of the Hermitage Museum in Leningrad began to elaborate the problem of restoration of modern tempera painting. They had examined a considerable range of materials that could be used for this purpose. Among the so-called natural materials, the resin and isinglass were put on trial. As a result, the conclusion was drawn that these materials could not be used for conservation of modern tempera paintings, because they provoke the darkening of pigments.

But undertaken tests had provided few brands of "ftorlons" (fluoroplasts) – synthetic material that could be applied for treatment of a damaged paint layer without consequent change of colour or texture of pigments. Fluoroplasts ("ftorlons") are the products of polymerization and copolymerization of fluoro- and olefins. This material is quite inert with respect to action to air, moisture and oxygen. Some paintings in tempera technique on different supports from the

Medieval Painting on Parchment: Technique, Preservation and Restoration

Hermitage collection with such destructions as pulverization of pigments were treated with ftorlon F-24L. The properties of this material are well known, as described in published articles. It is necessary to consider some of them. Ftorlons are applied in mixture of organic solvents. They cannot soften the deformations and hard cracks of the paint layer. So it is impossible to lay out the detached particles of pigments and to fix the paint layer with raised edges. This material may be applied successfully only when there is a lack of binding media in paints (in case of pulverization of pigments) and it is necessary to reinforce its structure. The absence of lustre and low index of refraction make for immutability of colour and texture of pigments after their treatment.

REINFORCEMENT OF THE PAINT LAYER ON PARCHMENT

So taking into account all shortcomings and technological particularities of natural glues, resins and other materials that are applied in conservation nowadays and after long-term experiments and practice we fixed upon an alcohol-water solution (2:1) of partially hydrolysed copolymer of vinylacetate with ethylene (CEV). We prefer the more elastic type with a degree of hydrolysis equal to 15%. Usually we use a 3% solution. It flows easily through detached particles of painting and immediately fixes them on the support; no displacements of them are observed. Fig. 4 and 5 may give an idea of its efficiency.

When a paint layer is moistened by a solution of polymer, the deformed parts of it begin to straighten themselves. No changes of colour and no halos around the treated parts appear, so that allows local treatment to be carried out more than once if it is necessary.

Two Russian chemists working in conservation, A. V. Ivanova and M. V. Yusupova, checked the properties of CEV as far back as 1979. They had noted that this material practically does not affect hygroscopic properties and moisture circulation of the parchment; film of CEV is easily removed by alcohol, and that does not require any specific precautions. Recently CEV films were tested on aging in a climatic chamber. These tests confirmed the stability of the properties of this polymer.

The process of fixing the paint layer with a solution of CEV is carried out under a microscope using different degrees of magnification (from $\times 6$ to $\times 25$) depending on necessity. That allows observation of how the solution passes inside the paint layer and helps to avoid some lapses. The solution is applied with a thin brush (no. 1 or 2) moistened in it. The brush touches gently the edges of damaged particles and cracked parts and solution penetrates easily



Fig. 4. Miniature from a Byzantine manuscript (15th century) "Akathistos to the Virgin" after treatment with a 3% alcohol-water solution (2:1) of partially hydrolysed copolymer of vinyl acetate and ethylene

under detached paints. And it should never be applied on the entire paint surface.

Applying that method, it is possible to introduce a minimal quantity of binding material. This method does not interfere in the structure of the painting; one can treat only the parts of it that are in a catastrophic state at the moment and are on the verge of complete loss.

We recommend drawing a scheme, where each treated section is registered. It facilitates observation of treated and untreated areas. The described synthetic material allows, if necessary, to repeat the treatment, also to undertake the process of distant moistening for straightening the deformations of parchment.

This method also makes possible to treat the miniatures without rebinding the manuscript. At the moment we consider our method for treating medieval miniatures on parchment effective enough and we don't see another version for this purpose.

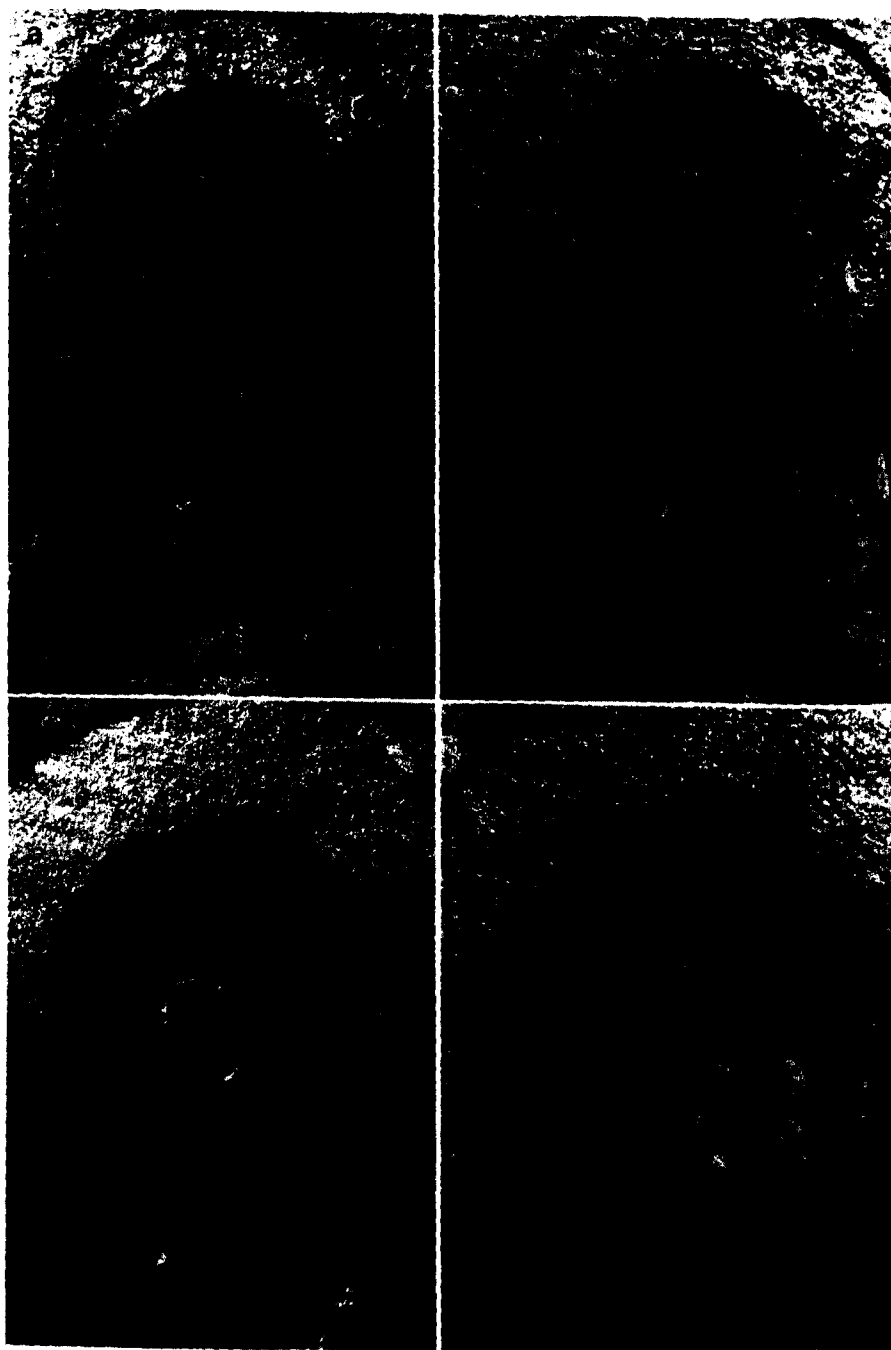


Fig. 5. Details from Fig. 3 and 4. Left (a and c): before treatment. Right (b and d): after treatment

SUPPLY

The two synthetic resins named in this article, ftorlon and CEV, are supplied by Plastopolymer, St. Petersburg, Russia.

SUMMARIES

Medieval Painting of Parchment: Technique, Preservation and Restoration

Different materials and sometimes opposite methods of Byzantine and Western miniaturists provoke different kinds of mutilation in the paint layer. The author analyses the mechanisms of these destructions and indicates the necessary conditions for treatment. She explains the inefficiency and sometimes impossibility of using natural materials for the treatment of painting on parchment. The Moscow Institute for Restoration and the newly organized Department for Conservation of Manuscripts in the Grabar Conservation Center have good experience with synthetic materials.

Peinture médiévale sur parchemin: technique de conservation et de restauration

Divers matériaux et parfois de méthodes opposées de miniaturistes Byzantins et Occidentaux provoquent différents types de mutilation dans la couche picturale. L'auteur analyse le mécanisme de ces destructions et indique les conditions nécessaires pour le traitement. Elle explique l'inefficacité et parfois l'impossibilité d'utiliser des matériaux naturels pour le traitement des peintures sur parchemin. L'institut de restauration de Moscou et le département de conservation des manuscrits récemment organisé dans le centre de conservation de Grabar ont une bonne expérience avec les matériaux synthétiques.

Mittelalterliche Malerei auf Pergament: Technik, Konservierung, Restaurierung

Verschiedenartige Materialien und bisweilen gegensätzliche Techniken in der Byzantinischen und der westlichen Buchmalerei sind die Ursache verschiedenartiger Schäden in der Malschicht. Es werden die Mechanismen des Abbaus und die notwendigen Maßnahmen zur Behebung diskutiert. Für Malerei auf Pergament ist die Anwendung natürlicher Festigungsmittel unwirksam und manchmal unmöglich. Das Institut für Restaurierung in Moskau und die neu eingerichtete Abteilung für Konservierung im Grabar Konservierungszentrum haben gute Erfahrungen mit synthetischen Materialien gemacht.

G. Z. Bykova
Grabar Conservation Center
Moscow
Russia

W93.14.3

Editorial Notice

RESTAURATOR, *International Journal for the Preservation of Library and Archival Material*, presents original papers, as well as reviews and news of interest to scientists, conservators, archivists, and librarians.

Authors submitting a paper do so on the understanding that the work has not been published before, is not being considered for publication elsewhere and has been read and approved by all authors. The submission of the manuscript by the authors means that the authors automatically agree to assign exclusive copyright to Munksgaard International Publishers if and when the manuscript is accepted for publication.

The work shall not be published elsewhere in any language without the written consent of the publisher. The articles published in this journal are protected by copyright, which covers translation rights and the exclusive right to reproduce and distribute all of the articles printed in the journal. No material published in the journal may be stored on microfilm or videocassettes or in electronic databases and the like or reproduced photographically without the prior written permission of the publisher.

Articles for RESTAURATOR are published in English, with Summaries (Abstracts) in French and German. However, manuscripts written in French or German are welcome, and will be professionally translated by Munksgaard. Contributors are particularly asked for linguistic and stylistic accuracy. All articles are linguistically revised by Munksgaard before publication. Authors alone are responsible for the opinions expressed in their articles.

Manuscripts should be provided on a floppy disk if possible; a printed, double-spaced copy must accompany any disk. Copy the files onto newly formatted disks and clearly label the journal, author and title, file content, originating machine and the word-processing program used. Manuscripts must be carefully revised, as alterations are expensive. The paper must be non-absorbent. The author's name must be accompanied by the title, full address, telephone and telefax number (if any) of the workplace or institution. Summaries should be written on a separate page, included with the manuscript; should not exceed 200 words; and should be written in the same language as the articles.

All graphs, drawings, or photographs are to be referred to as figures (abbr: Fig.) and should be numbered in sequence with Arabic numerals. Each figure should be identified with a figure number on the back. Any lines, numbers, or lettering that are to appear in the illustrations should be large enough for the necessary reduction. Line drawings should be drawn with black India ink on white paper and should be about twice the size of the finished blocks. Graphs can be plotted on plain white or blue squared paper; grid lines should be inked in black. In general, photographs should be about 1½ times the size of the final block and must be submitted as mounted glossy enlargements showing good detail and adequate, but not excessive, contrast. Authors should indicate in the text the approximate position of figures.

Italics are used for emphasis, especially for distinguishing titles of books and papers.

References within the text should be indicated by numbers corresponding to those in the list of references. The list should be placed at the end of the paper. For example:

1. Miles, C.: *Wood coatings for display and storage cases*. Studies in Conservation 31 (1986): 114-24.
2. Hon, D. N.-S.: *Yellowing of modern papers*. In: Williams, J. C., ed. *Preservation of paper and textiles of historic and artistic value II*. Advances in Chemistry Series, 193. Washington, DC: American Chemical Society, 1981: 119-42.

Fifty offprints of each article will be sent to the author free of charge. Extra copies, if desired, will be supplied at a special rate.

©1993 Munksgaard International Publishers Ltd. Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by Munksgaard International Publishers Ltd. for libraries and other users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service, provided that the base fee of USD 6.00 per copy is paid directly to CCC, 27 Congress Street, Salem, MA 01970. 0034-5806/93/USD 6.00 + 0.00. All other rights, including microfilm, reserved.

Editorial Address

Manuscripts and review copies of books should be sent to the editorial office: RESTAURATOR, Dr. Helmut Bansa, Elisabethstraße 23, D-80796 Munich 40, Germany.

RESTAURATOR

Contents 14:3

- 123: M. G. VINE & W. K. HOLLINGER: Active Archival Housing
131: M. LEROY & F. FLIEDER: The Setting of Modern Inks Before
Restoration Treatments
141: M. MARAVAL & F. FLIEDER: The Stability of Printing Inks
172: R. MOROZ & E. ROEVER: A New Approach to Systematic Dry
Cleaning with Technical Devices
188: G. Z. BYKOVA: Medieval Painting on Parchment: Technique, Preser-
vation and Restoration

Indexed in:

Chemical Abstracts

Current Contents

Information Science Abstracts

Library Literature

Library Science

Social and Educational Science

Citation Index

Printed in Denmark by P. J. Schmidt A/S, Vojens.

ISSN 0034-5806