Quality Control and Optimization of the Conservation Treatments applied to the material of the Archives of KKE (Greek Communist Party).

by A. Moropoulou, S. Zervos, P. Mavrantonis.

This is an edited version of the originally submitted manuscript (prerefereed) of the article: "Quality Control and Optimization of the Conservation Treatments applied to the material of the Archives of KKE (Greek Communist Party)" by A. Moropoulou, S. Zervos & P. Mavrantonis, published in Restaurator, Volume 22, Issue 3, Pages 146–163, ISSN (Print) 0034-5806, DOI: 10.1515/REST.2001.146, /September/2001

The original publication is available at:
http://www.reference-global.com/doi/abs/10.1515/REST.2001.146

1. INTRODUCTION

This study presents the quality control of the conservation treatments applied to the paper of the Archives of KKE, mainly of the deacidification treatment with calcium hydroxide solution in water[1]. Among the targets of this study is to suggest a reliable, simple and relatively inexpensive procedure for the quality control of conservation interventions in general, which can be carried out in a more or less well organized Archival institution or Library.

The methodology and the methods used for the evaluation of conservation treatments on paper come originally from the paper industry[2]. Table 1 presents the most common tests. In the majority of such studies, a big number of time consuming and expensive tests is carried out. Folding endurance, tensile properties and bursting strength are very often used together for the evaluation of the mechanical properties of paper and in both directions of paper (machine direction and cross direction). The results are often contradictory and confusing.

It has been suggested[3] that a limited number of tests should be applied and in only one direction of the paper samples. In this framework, only one mechanical, one chemical and one optical fundamental property would be investigated in the present study. Complementary to them, the fibre optics microscope would be used for the examination of the structural properties of the paper and the precipitation pattern of the deacidification agent.

	METHOD	ISO	OTHER RELATED STANDARD
1	Tearing Resistance	1974	CPPA D. 9, TAPPI T 414 m-49
2	Folding Endurance	5626	CPPA D. 17P TAPPI T511, TAPPI T 423 su-68
3	Tensile Properties: 1 Constant Load, 2 Constant Elongation	1924-1 1924-2	CPPA D. 34, DIN 63112, TAPPI T494
4	Bursting Strength	2758	TAPPI T403 m-55
5	Tensile post fold		
6	Zero span tensile strength		
7	ISO Brightness	2470	CPPA E. 1
8	Colorimetry (CIE Lab)		ASTM D 2244 - 93
9	Water Absorption	5637	
10	pH of aqueous extracts Cold or warm extraction	6588	CPPA G. 25P , TAPPI T435 om 88, TAPPI T509, TAPPI T-428, ASTM D-542, DIN 53124, NEN 2151
11	Alkali Reserve	10716	TAPPI T 428, ASTM D 548, ASTM D 4988 – 89, ANSI PH 1.53 - 1978
12	Kappa number	302	
13	Standard test method for intrinsic viscosity of cellulose (DP)		ASTM 1795 – 90 Afnor NFT 12-005
14	SEM (Scanning Electron Microscope) – EDX (X – Ray Microanalysis)		
15	FTIR (Fourier Transformation Infra Red Spectroscopy)		
16	Water soluble Cl^- (Potensiometric titration)	9197-1	
17	TLC (Thin Layer Chromatography)		
18	Fibre furnish Analysis Staining guide Optical Microscopy	9184-1 -2, -3, -4, -5, -6, -7	TAPPI T401, om-88, TAPPI T263 om-82, TAPPI T259 om-33, ASTM D1030
19	Carboxyl content		ASTM 1926 - 89
20	Copper Number (i cu)		Afnor NFT 12-004, TAPPI T 430, ASTM D919
21	Lignin content		TAPPI T 222
22	A-cellulose content		TAPPI T 203 os-74, TAPPI T-429, ASTM D-588
23	Accelerated Ageing	5630 – 1, 2, 3, 4	TAPPI T 453 ts-63, ASTM D 776
24	Conditioning (23°, 50% RH)	187	ASTM D685-87, TAPPI T 402
25	Grammage Determination	536	
26	Dry matter determination	287	
27	Moisture content		ASTM D1348-89
28	Thickness		TAPPI T411

Table 1: The most common tests used for the evaluation of paper conservation treatments

2. THE CASE OF THE KKE ARCHIVES

The Historical Archives of KKE (Greek Communist Party) are housed in the headquarters of the party at Perisos, Athens. They consist of about 30,000,000 pages and include every kind of written and printed material - books, newspapers, periodicals, announcements, propaganda sheets, posters, manuscripts, mimeograph prints, letters, ledger books etc, spanning from the beginning of the 20th century until today.

In October 1994, as the result of a heavy rainstorm, the basement of the headquarters of KKE, where the Archives were kept, flooded. Mud and refuse, washed by the rain, covered the material of the Archives and the danger of their total destruction was visible.

Six years have passed since then and the situation today is completely different. Conservation treatments and preservation measures have been implemented, triggered by the flood, in order to save the Archives. The Sector of Material Science and Engineering (SMSE) of the Chemical Engineering Faculty of the National Technical University of Athens undertook the planning of the interventions. Recognizing that the most important internal factor accelerating the ageing of paper is its acidity, deacidification was proposed as the main paper conservation treatment intended to stabilize it chemically.

The most feasible deacidification method appeared to be the treatment with calcium hydroxide solution in water, because of its simple application and low cost. One must bear in mind that there were no specialized personnel available and everything depended on volunteers. Therefore, the method had to be easy to apply, not implementing sophisticated chemicals and equipment.

Directly after the flood, the wet and soiled material was placed in freezers (-10°C) to avoid fungi growth. When decisions were made and everything was ready for coping with the situation, material was taken out of the freezers in batches, washed to remove the biggest part of the mud, air-dried and disinfected with T-gas (ethylene oxide 90% - carbon dioxide 10%). Microbiological examination manifests that after disinfection fungi were killed. All the material of the Archives has been subjected to these stages and now is securely stored in a specially designed room (600 m^2), air conditioned (RH = 50-60%, T = 16-18°C) and ventilated. A significant part of it has already been deacidified (over 15%).

Deacidification procedure[4] is as follows:

1. Prewashing in lukewarm (up to 40°) running tap water, until the water stops becoming yellow (at least for 45 min.)
2. Immersion in saturated calcium hydroxide ($Ca(OH)_2$) solution in water for 20 min.
3. Air-drying
4. Random pH testing (desired pH between 8 - 8.5).
5. Storing of deacidified paper in archival quality envelopes that are kept in the specially designed room.
6. This procedure is applied to batches of paper in big inox vats. Plastic grid is used for the support of the fragile wet paper during wet treatments and drying.

3. EXPERIMENTAL

3.1. SAMPLES

It was decided that blank[5] historic paper should be used for samples. The Archives of KKE provided 30 leaves of paper[6]. These leaves constituted 4 sample series (A, B, C and D series). The quality of paper of every series was identical. This was ensured by taking the 8 leaves of a series from the same archival file and verified by macroscopic observation. Unfortunately, not all of the paper provided by KKE could be used for samples.

Furthermore, the quantity of paper was not enough and more samples were needed. The paper from the margins of 3 books, contemporary to the Archives of KKE was used as additional samples (E, F, and G series). The paper of the sample series A, B, C and D was of poor quality and preservation status, not uniformly colored but full of stains, creases and discolorations. On the contrary, the paper of the series E, F and G was uniformly colored, of medium quality and better condition[7].

	1st group	2nd group	3rd group	4th group	
Process	R	A	T	TA	PULP TYPE
Leaves	1 & 2	3 & 4	5 & 6	7 & 8	
A (1935)	AR	AA	AT	ATA	MP
B (1940)	BR	BA	BT	BTA	MP
C (1950)	CR	CA	CT	CTA	CP
D (1965)	DR	DA	DT	DTA	MP
E (1909)	ER	EA	ET	ETA	CP
F (1944)	FR	FA	FT	FTA	CP
G (1956)	GR	GA	GT	GTA	CP

Table 2: Table illustrating the grouping of samples according to their processing. The number of leaves refer to the sample series A, B, C and D. Therefore, the sample D7 or DTA7 is the 7th leave of the D series, which has undergone conservation treatment (T) and ageing (A). (R: Reference, A: Aged, T: Treated, TA: Treated and Aged MP: Mechanical Pulp, CP: Chemical Pulp)

3.2. TECHNIQUES AND METHODOLOGY

The basic concept behind every work attempting to evaluate the efficacy of methods and materials used in paper conservation is the comparison of the degradation rate of the mechanical, chemical and optical properties of the treated and untreated paper in the course of time[8]. In order to make this comparison possible and extract conclusions without having to wait for many years so that the properties of the treated and untreated paper differentiate, a method of accelerating the ageing of paper is necessary.

In this study, dry *accelerated ageing* at 105°C was chosen (ISO 5630-01)[9], mainly because of the convenience of its application[10]. A simple desiccator was adjusted at 105±2°C and the paper samples were hung from wires, leaving a space of at least 1 cm between them for the air to circulate evenly. A period of 3 days seemed to be the best choice of ageing time[11], but as colorimetry indicated, the treated and untreated samples had not differentiated sufficiently after that period of time. Thereby, the ageing process continued for another 3 days. This time, the colorimetry results were satisfactory. Colorimetry was used as an indicator of the efficacy of accelerated ageing because it was the only non-destructive method available that could give information about the chemical degradation of the samples.

Three paper properties were selected for comparison before and after accelerated ageing[12]:

- Mechanical properties: *Folding Endurance* (ISO 5626)[13]

FE was selected because it represents paper usability better than other mechanical properties. Furthermore, it is very sensitive in accelerated ageing[14]. A Kolher – Molin type instrument made by Lorentzen & Wettres was used. The samples were left to acclimatize in the testing room before measurements were taken. The load was 7.85 N (800 gr). 10 strips (10x80mm) were cut in the directions of the paper sheets (machine direction or cross direction) that could give the most strips[15].

- Chemical Properties: *pH of cold aqueous extract* (ISO 6588)[16]

pH was selected since it is the chemical property that mostly influences the ageing stability of paper. The paper strips used in the previous test were reused for measuring the pH. 2 gr (oven dry basis) of paper were cut in small pieces (5x5 mm), weighed (0.01 gr precision) and extracted for an hour with 100 ml of twice distilled water (Merck).

- Optical Properties: *L* and b* coordinates of the CIEL*a*b* (1976) color system*[17]

Aqueous treatments of paper result in washing and removing of colored degradation products, thus increasing the brightness and reducing the yellowness of the paper (cleaning). On the other hand, alkaline catalyzed lignin oxidation – occurring in the highly alkaline deacidification bath (pH ≈ 12) – produces colored compounds (such as stilbenes and quinones[18]) that absorb blue light, thus give a yellow hue to paper, reducing brightness and increasing yellowness. Ageing too, natural or accelerated, produces yellow - brown compounds (by direct oxidation of the paper components or by oxidation of the cellulose, lignin and hemicelluloses degradation products), which again increase yellowness and reduce brightness of paper. For the above reasons, L* (luminance or lightness, equivalent to brightness) and b* (position on the blue-yellow axis, indicating the degree of yellowness) coordinates of the CIEL*a*b* color system are considered of major importance because they quantify the above-mentioned trends.

A Dr. Lange Color Pen LMG 159/160 colorimeter with precision ±0,1 was used. For the uniformly colored samples (E, F, G series), the average of 5 measurements in specific book pages is presented. For the non-uniformly colored samples (A, B, C and D series), 5 measurements were taken in two specific spots of every paper leaf (α and β) and the average of every spot is presented. In order to accurately specify the spots, masks were cut from plain photocopy paper and applied to the samples. The tip of the colorimeter was traced with pencil on the masks (fig. 1).

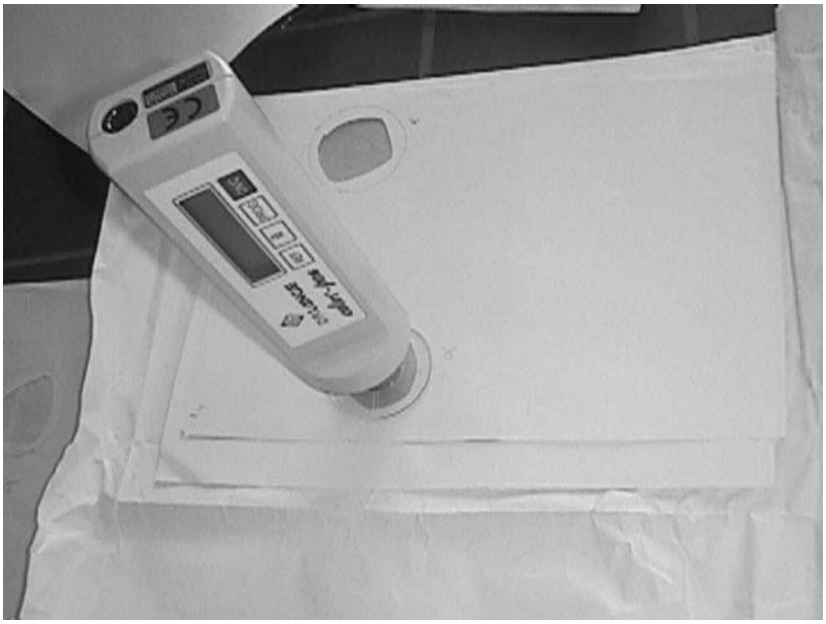

fig.1: How the color measurements were taken for the non-uniformly colored samples

Phloroglucinol spot test[19] was carried out in order to categorize the samples according to the kind of the pulp used in their manufacture (Table 2). Positive test (red shade) indicated the presence of lignin, which is a major constituent of mechanical pulps. Negative test indicated no detectable quantities of lignin. In this case the paper was made of chemical pulp.

In order to determine how the deacidification agent was deposited, a *fibre optics microscope* (FOM) was used. FOM is a small, portable video camera. Lenses of various magnifications (from x10 to x600) can be used with it. It can be connected to a P/C via a video capture interface and the pictures taken can be saved in *jpg* format, enabling further processing. FOM has been used in the laboratory of the SMSE for the evaluation of cleaning interventions and consolidation of architectural surfaces and this is the first time it is used for the evaluation of paper conservation treatments[20, 21].

Each series of samples was divided in 4 groups: Reference (untreated) – Aged - Treated - Treated and Aged. Therefore, 4 series of measurements were taken for every property, except for color. For color measurements, the same sample was used to acquire 2 (reference and aged or treated) or 3 (reference, treated and treated and aged) series of measurements, depending on the treatment of the specific sample. The order of the execution of the tests was: CIEL*a*b*⇒ Folding Endurance ⇒ pH and the paper strips used for the measurement of the FE were reused in the pH measurements. This was done in order to use as little paper as possible, since the paper available was marginally scant. The flow chart of fig. 2 depicts the above procedure schematically. The standard deacidification procedure was applied to the "treated" samples at the conservation laboratory of the Archives of KKE.

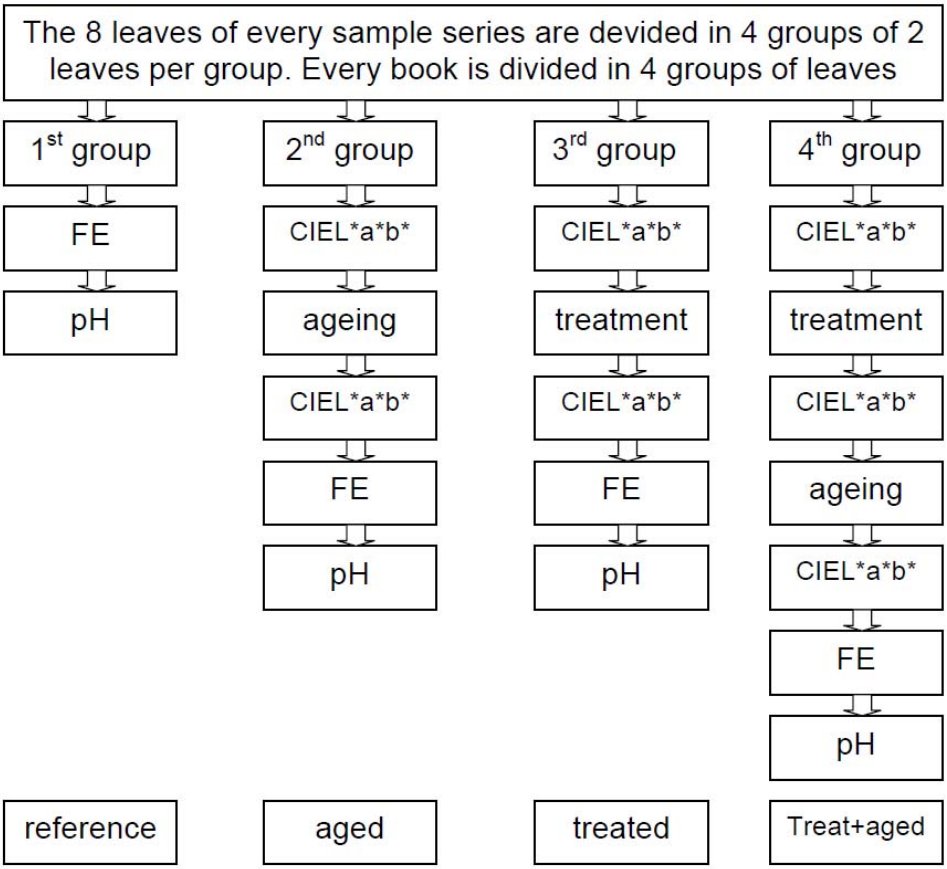

fig.2: Flow chart of the experimental procedure

4. RESULTS

4.1. FIBER OPTICS MICROSCOPE

All FOM pictures manifest that a part of the alkaline reserve is deposited as large crystals on the surface of the paper (fig. 3). This is considered to be a disadvantage of the method, because the deacidification agent is not uniformly distributed in the paper[22] and the large crystals can cause abrasion on the surface.

The fibre optics microscope has been proved to be a very efficient tool for the structural examination of paper, offering sufficient magnification and convenience of use since it is portable and the samples need no preparation.

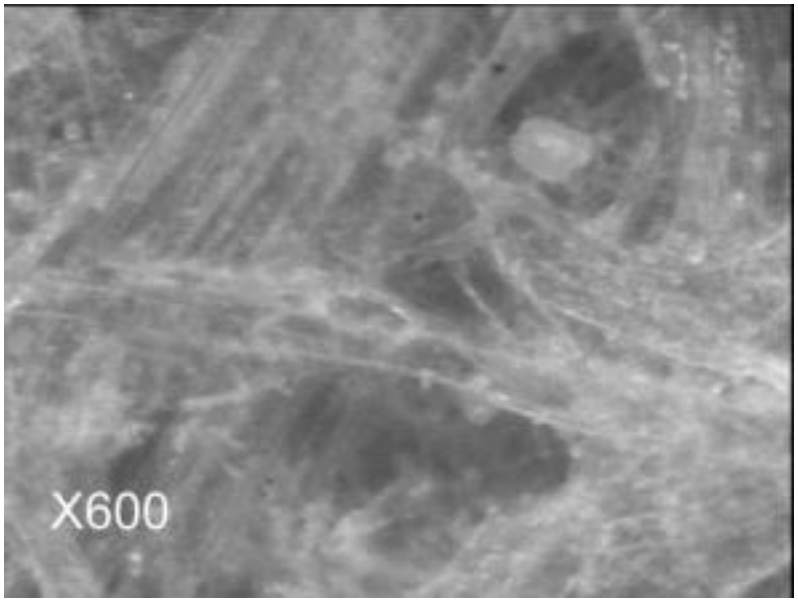

fig.3: Large crystals of alkaline reserve are deposited on the surface of the paper

4.2. FOLDING ENDURANCE

Loss of strength due to ageing is greater for the untreated samples. Four out of five samples exhibit increased strength compared to the reference as a direct result of the treatment. This most probably happens because of the rearrangement of the cellulose chains and the regeneration of the broken hydrogen bonds among them[23].

The sensitivity of the method towards accelerating ageing was reconfirmed. According to fig. 4, the behavior of the samples exhibited satisfactory differentiation and therefore conclusions could be drawn.

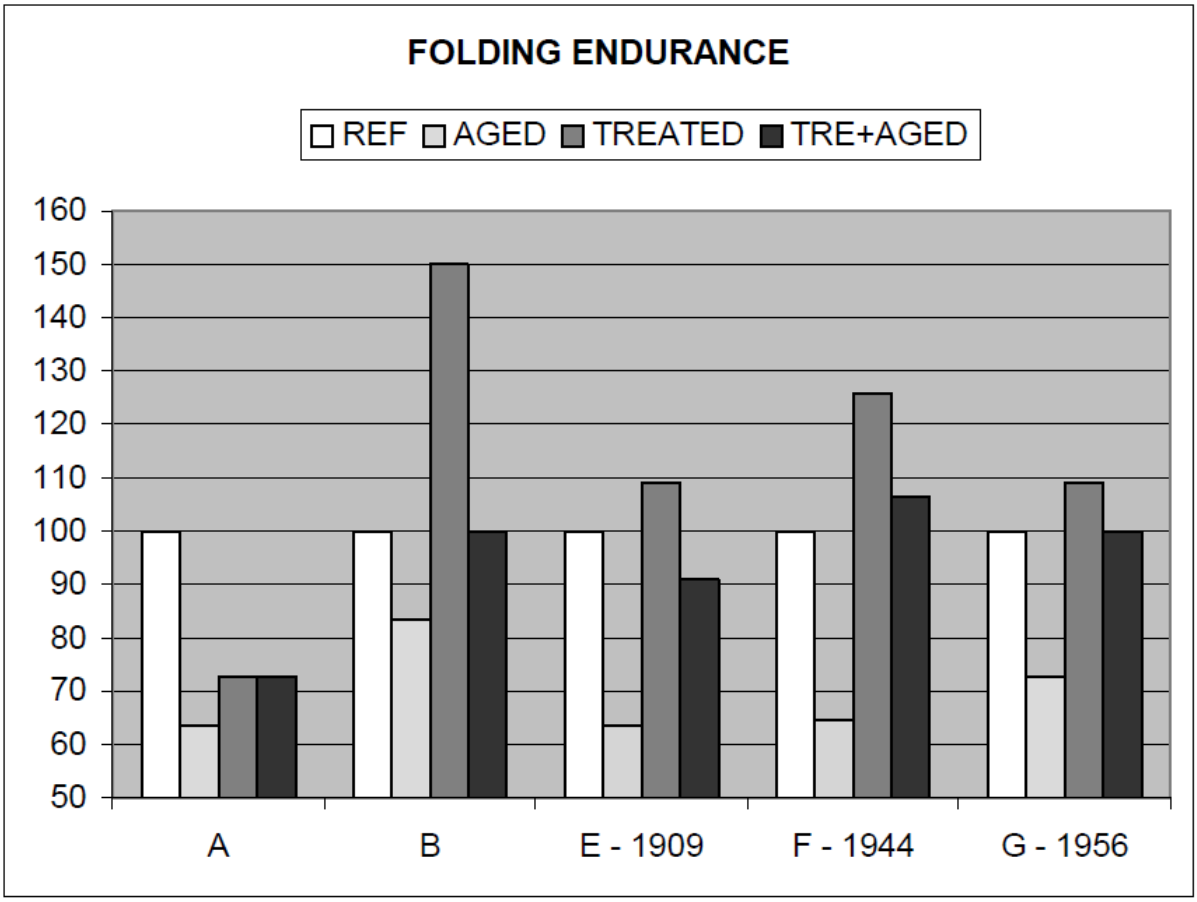

fig. 4: Graph of the number of double folds (normalized, ref=100)

4.3. pH OF THE COLD AQUEOUS EXTRACT

Deacidification increased the pH of the samples from 1.5 to 3.5 units (fig. 5). The pH values measured after deacidification do not exceed 8.5. 8,5 – 9 is considered to be the threshold where the alkaline catalyzed autoxidation of cellulose starts[24]. Ageing caused only a slight decrease in pH, leaving it in the alkaline region.

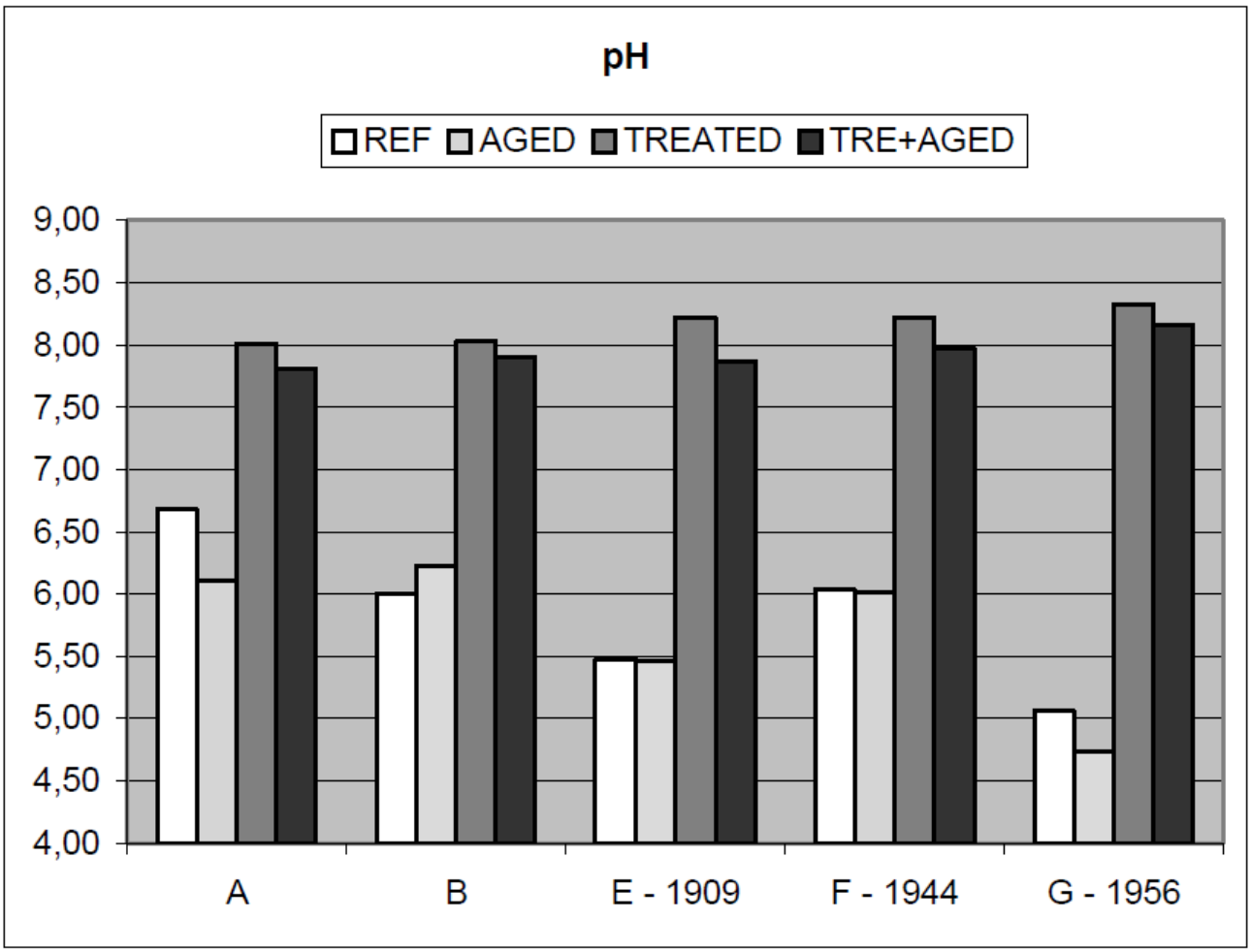

fig. 5: pH graph

5. COLORIMETRY (CIEL*a*b*)

The rate of the decrease in lightness (L*) and the increase in yellowness (increase of b*) – ageing rate – is less for the deacidified samples (fig. 6, 7, 8, 9).

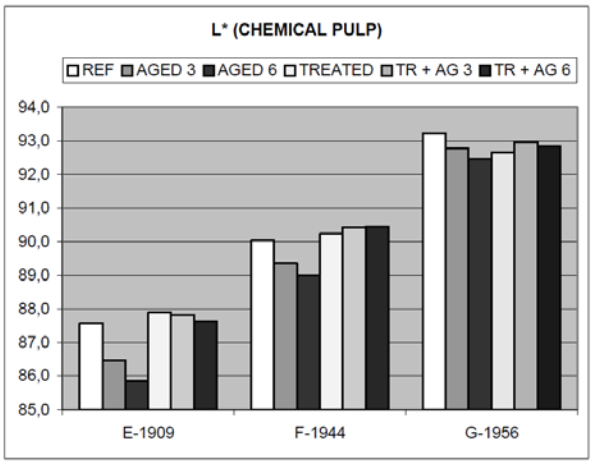

fig. 6: Lightness of samples E, F and G

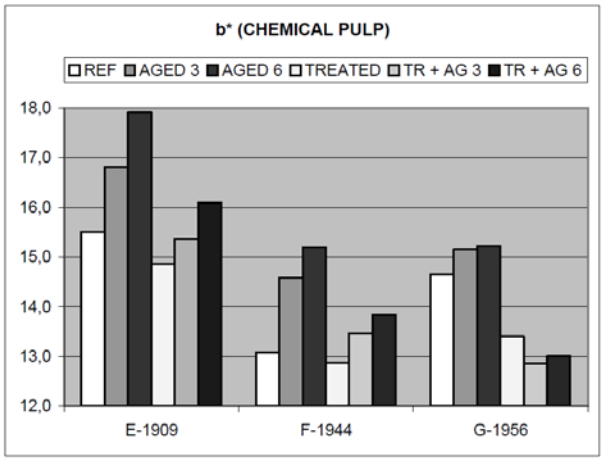

fig. 7: b coordinate of samples E, F and G

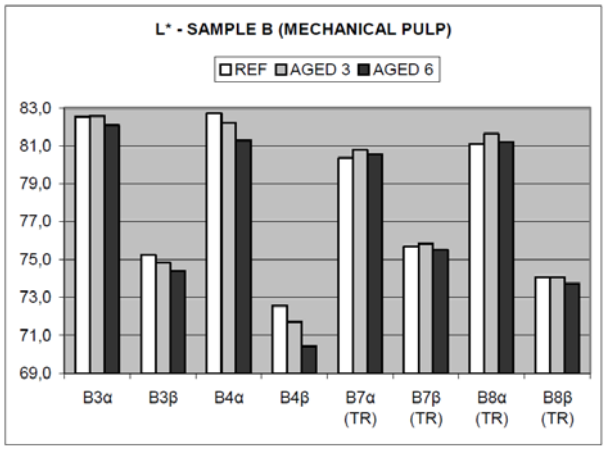

fig. 8: Ageing rate of sample B, as indicated by the reduction of L*. For treated samples (TR), reference (REF) is the treated

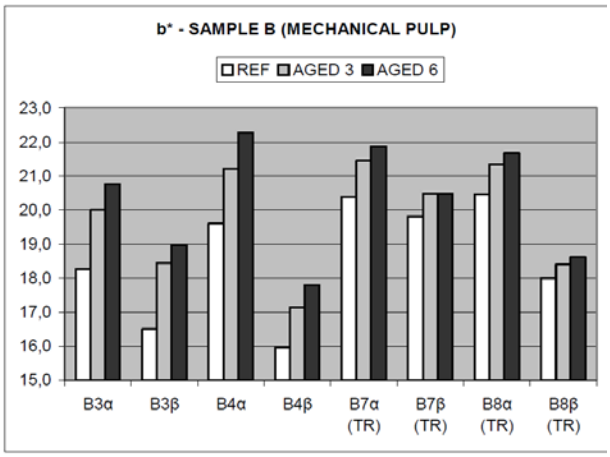

fig. 9: Ageing rate of sample B, as indicated by the increase of b*. For treated samples (TR), reference (REF) is the treated

Comparison of L* and b* between REF and TREATED in fig. 6 and 7, which shows the immediate results of the deacidification on the color of the samples made of chemical pulp, indicates that as far as L* is concerned there is no significant change; on the other hand, the decrease of b* indicates that colored degradation compounds are removed (cleaning).

Fig. 10 shows the lightness of sample B (made of mechanical pulp) before and after deacidification. It indicates that lightness increases at places where rust stains are, since water removes colored substances and decreases elsewhere because of the oxidation of lignin in the highly alkaline deacidification bath. The oxidation of lignin is responsible for the overall yellowing of the sample (increase of b*, fig.11). The samples A and D (colorimetry results for these samples are not presented here) exhibited the same behavior as sample B.

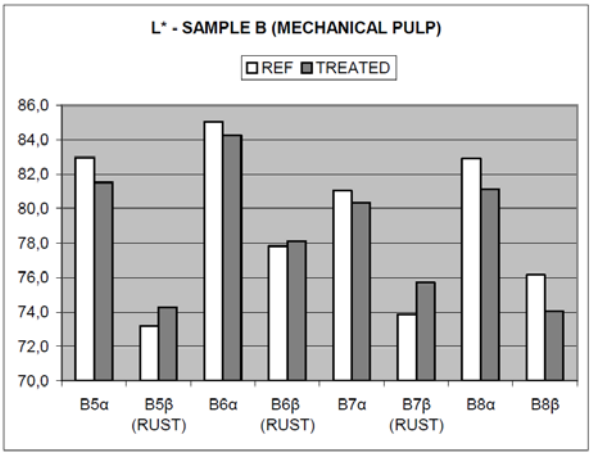

fig. 10: Effect of the deacidification on the lightness of the sample B

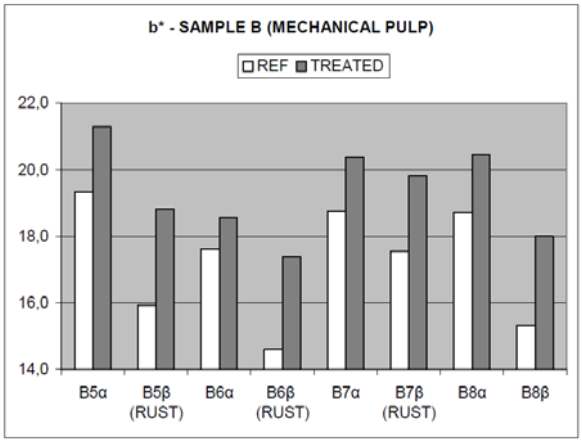

fig. 11: Effect of the deacidification on the b* coordinate of the sample B

6. ELABORATION OF RESULTS BY PRINCIPAL COMPONENT ANALYSIS

Principal Component Analysis (PCA)[25, 26] was used in order to examine if the variables measured in this study are statistically correlated. Although not a routine method for data statistical analysis, PCA has been used successfully in many fields. It is utilized in the laboratory of SMSE for the examination of the correlation between crusts and degradation products of architectural surfaces and their causes[27, 28]. This is the first time it is used for the investigation of the correlation among paper properties.

PCA could only be applied to the data pertaining to the sample series E, F (Z in fig. 12) and G (H in fig. 12), because every sample has one and definite value attributed to every variable. This is not the case for the samples of the A, B, C, and D series, where every sample is non uniformly colored and there is no definite value for the color coordinates L* and b*. This is not a deficit of PCA or the experimental procedure but merely an inherent attribute of historic paper.

As one can see from the plot of the principal components (fig. 12), there is a significant relation between L* and FE and a significant inverse relation between b* and FE. pH is not correlated significantly to any other variable.

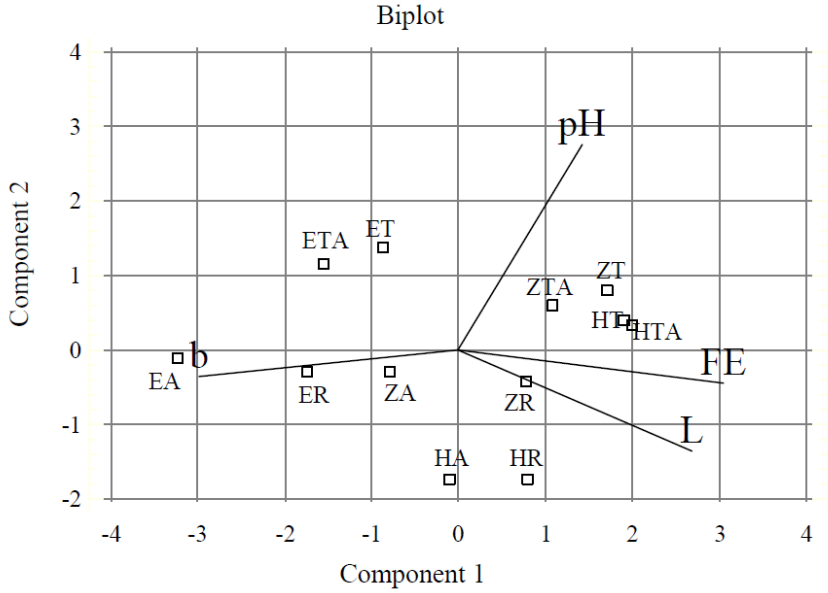

fig. 12: Percentage of variance explained, Component weights and plot of the variables pH, b, FE and L

The correlation coefficient between FE and b* was calculated and was found to be equal to –0.88 (P-value=0.0001). Since the P-value is less than 0.01, there is a statistically

significant relationship between FE and b* at the 99% confidence level. *One must bear in mind that this relationship was found for the non-lignin containing samples.*

7. DISCUSSION

7.1. TECHNIQUES, CRITERIA AND METHODOLOGY FOR THE QUALITY CONTROL OF THE CONSERVATION TREATMENTS

It is believed that the experimental procedure followed in this study can be implemented for routine quality control of the conservation treatments in a fairly well organized institution, since it is relatively quick, convenient and inexpensive and can give clear-cut results:

- Six days of dry accelerated ageing can sufficiently differentiate treated and untreated samples and can be done easily and inexpensively.
- Fibre Optics Microscopy can give information for the precipitation pattern of the deacidification agent and for structural changes. It is non destructive and can be applied in situ.
- Folding Endurance is very sensitive in accelerated ageing and treated and untreated samples differentiate significantly.
- pH measurements exhibit significant differentiation of the treated and untreated samples.
- Colorimetry can be used as an indicator of the efficiency of accelerated ageing before applying destructive tests on the samples. It gives valuable results concerning the aesthetics and the degree of chemical deterioration of the samples.

The deceleration of the deterioration of the paper properties after the conservation treatment was the general criterion for declaring a treatment as successful. Other minor criteria were:

- Improvement of the measured property after treatment
- Uniformity of precipitation of the deacidification agent
- Small sized crystals of the deacidification agent on paper
- pH after deacidification between 7 and 8.5
- pH after deacidification and ageing in the alkaline region
- Increase in lightness (higher L*) and decrease in yellowness (lower b*)
- No alterations in the appearance of the treated samples

7.2. SUITABILITY OF THE CONSERVATION TREATMENT

- Quality control showed a significant improvement of the ageing rate of the treated samples. The mechanical properties were improved and the pH of the treated samples was well in the alkaline region and remained there after accelerating ageing. The overall assessment of the conservation treatment is positive with two exceptions concerning the aesthetics:
  - The color of the lignin containing samples deteriorated. The yellowing of these samples is attributed to the highly alkaline deacidification bath that caused lignin oxidation with the subsequent production of yellow substances that were insoluble in water and could not be removed in the deacidification bath. The color difference[29] was calculated and found to be between 1.3 and 5.7, exceeding in many cases the limit value of 2 over which the color differences are discernible by the human eye[30]. Nevertheless, for one to see the difference, the samples have to be put side by side. If not, the difference is not that big to be noticed. That is why the color deterioration is not considered to be a major problem.
  - The deacidified papers are air-dried on plastic grid. This is the typical procedure at the KKE Archives. Observation of the treated samples revealed that the mark of the plastic grid is imprinted on fairly many sheets of paper (fig. 13). This fact, is considered to be of major importance, concerning not only the aesthetics. It is suspected that the gridline marks consist of wet-dry interfaces formed as the paper

dried, where cellulose has been oxidatively degraded[31]. The places where the grid was in contact with the paper dried last, forming the dark lines.

- The results of the PCA indicate that for rag or chemical pulp made paper (with no lignin component), the color coordinates L* and especially b* is strongly related to folding endurance. This implies that the more yellow a paper is, the less usable it is, which is what common sense tells. This fact, if confirmed by further investigation, could be exploited in paper condition surveys, as the measurement of b* is very easy and quick and most importantly, non destructive.

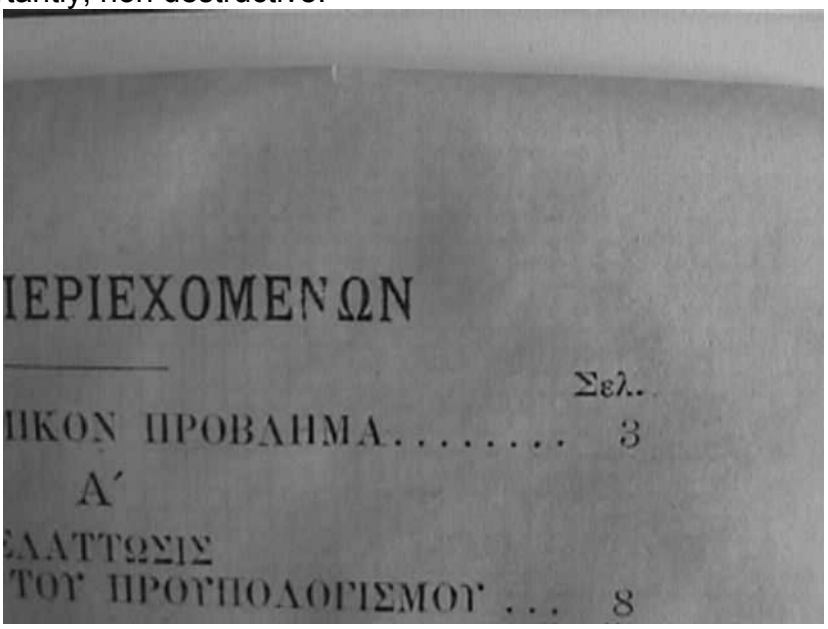

fig. 13: The grid imprint on a sheet of paper.

7.3. SUGGESTIONS FOR THE OPTIMIZATION OF THE TREATMENT

- The deacidification treatment with saturated calcium hydroxide solution was applied to treated and untreated by the KKE samples, following a slightly different procedure at a different paper conservation laboratory. 4 prewashings were applied, with tap water of ambient temperature for half an hour each. Spaying the samples with a 50% ethanol solution preceded prewashing. Colorimetry reconfirmed[32] that spraying the dry paper with a 50% ethanol solution and prolonging the prewashing period results in better removal of colored compounds. It is thus recommended:
  - Spraying with 50% ethanol before prewashing
  - Prewashing for longer time
  - Pressing the batch of paper from time to time during prewashing
  - Reduce the quantity of papers treated in one batch
- The use of Holytex or other non-woven polyester tissue is strongly recommended as a replacement for the plastic grid used for support during washing and drying of the paper. It will increase the cost of the treatment but it will reduce the possibility of accidents during washing and will definitely improve the appearance (and probably the life expectancy and durability) of the paper, since there will be no signs of the grid.
- If paper dries under slight pressure, cockling is avoided. It is then recommended to use 4 weights of 0.5 – 1 Kg each at the 4 corners of a board to press the drying papers. Interleaving with Holytex tissue and blotting paper is necessary. 20 to 30 leaves of paper can dry this way in a pile.
- Replacing the deacidification agent (calcium hydroxide) with calcium bicarbonate should be considered[33], since calcium bicarbonate is more soluble in water than calcium hydroxide[34] and the pH of the saturated calcium bicarbonate in water is about 6. The low pH value denotes that there will be no lignin oxidation problem, so there will be no or at least less paper discoloration.

- KKE should consider installing a small-scale mass deacidification treatment plant, since the quantity of the material to be deacidified is huge. The existence of contemporary inks that bleed in water could be another reason for doing so, since inks could be stable in the non-aqueous solvents used in mass deacidification. This matter needs a thorough investigation that exceeds the scope of this study.

8. CONCLUSIONS

The results of this study manifest that:

- The techniques, criteria and methodology used have been proved to be suitable for routine quality control of conservation treatments. Six days of accelerated ageing can effectively differentiate treated and untreated paper. Folding endurance, lightness (L*) and yellowness (b*) and pH represent fundamental mechanical, optical and chemical properties of paper and are sufficiently sensitive in accelerated ageing. FOM can be used instead of optical microscope for the structural examination of paper with good results. The main criterion for declaring a treatment as successful was the decrease of the deterioration rate of paper properties due to the conservation treatment.
- The conservation interventions applied to the material of the KKE Archives were successful, as quality control indicated.
- The application of minor alterations (spraying with alcohol solution before prewashing and the use of non-woven polyester tissue) can optimize the deacidification procedure.

REFERENCES

[1] Master Thesis by Zervos, S., approved by the Chemical Engineering Faculty of the National Technical University of Athens, 2000, entitled: *Investigation of criteria and methods for the evaluation of the suitability of conservation interventions on archival material in relation to the planning of the conditions of the surrounding environment (application on the Historical Archives of KKE),* supervised by A. Moropoulou.

[2] For a detailed description of test methods applied in the paper industry see: Grant, Julius, *A Laboratory Handbook of Pulp and Paper Manufacture*, London, Edward Arnold (Publishers) LTD, 2nd edit., 1961.

[3] Bansa, H., *Accelerated Ageing Tests in Conservation Research: Some Ideas for a Future Method*, Restaurator, 13:3, 1992, p. 135,136

[4] Greek Communist Party (KKE), responsible group for the conservation treatment: P. Gontikas (political head), P. Mavrantonis (scientific head).

[5] The paper would be weaker at the places where it was printed or written, resulting in unreliable strength measurements. This problem was encountered by Green et al, see Green, L. R. & Leese, M., *Nonaqueous Deacidification of Paper with Methyl Magnesium Carbonate*, Restaurator 12:3, 1991, p.152, 159.

[6] 72 leaves of paper (size A4 or equivalent quantity) were initially requested from KKE (3 sample series per period x 3 periods of time x 8 sheets per sample). The request was not met, because of the inability of KKE to find sets of 8 sheets of paper of identical quality.

[7] Some samples of good condition were necessary for the measurement of the folding endurance. Mechanical properties could not be reliably measured in non-uniform samples.

[8] Bansa, H, op. cit.

[9] International Standard: ISO 5630-1: Paper and board – Accelerated ageing – Part 1: Dry heat treatment at 105 °C, 1991.

[10] Bansa, H, op.cit.

[11] Three days is the least ageing time encountered in bibliography that can cause measurable changes in the properties of most kinds of papers, see also: International Standard: ISO 5630-1: Paper and board – Accelerated ageing – Part 1: Dry heat treatment at 105 °C, 1991

[12] Bansa, Helmut, *Aqueous Deacidification - with Calcium or with Magnesium*, Restaurator, 19:1, 1998, p. 6.

[13] International Standard: ISO 5626: Paper – Determination of folding endurance, 1993.

[14] International Standard: ISO 5630-1: Paper and board – Accelerated ageing – Part 1: Dry heat treatment at 105 °C, 1991.

[15] A significant quantity of paper of some sheets (from sample series A, B, C and D) had to be rejected, since it was unusable because of holes, creases and rust stains. All the measurements of the same series were taken in the same direction.

[16] International Standard: ISO 6588: Paper, board and pulps – Determination of pH of aqueous extracts, 1981.

[17] ASTM STANDARD D 2244 – 93: Standard Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates, 1993.

[18] Dence, C., Reeve, D., *Pulp Bleaching, Principles and Practice*, Atlanta, Georgia, Tappi Press, 1996, p. 95.
[19] Grant, Julius, op. cit., p.377.
[20] A. Moropoulou, M. Koui, Th. Tsiourva, Ch. Kourteli, D. Papasotiriou, *Macro – and micro non destructive tests for environmental impact assessment an architectural surfaces*, Materials Issues in Art and Archaeology IV, edited by J.R. Druzik and P.B. Vandiver, Publ. Materials Research Society, (1996), in press. (ci: AATA)
[21] A. Moropoulou, G. Biscontin, Th. Tsiourva, K. Bisbikou, P. Longega, V. Tsantila, M. Groggia, E. Dalaklis, A. Petritaki, *Evaluation of cleaning procedures on the facades of the Bank of Greece historical building in the centre of Athens*, 4th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Conference Proceedings, edited by A. Moropoulou, F. Zezza, E. Kollias , I. Papachristodoulou, Publ. Technical Chamber of Greece, Rhodes, Vol. 4, (1997), σελ. 343 – 354.
[22] Uneven distribution of the deacidification agent can create areas that will be more vulnerable to acid hydrolysis in the future. Thus, differences in color and strength may develop.
[23] Lienardy, Anne, Van Damme, Philippe, *Paper washing*, The Paper Conservator, 14, 1990, p.27.
[24] Kolar, Jana, *Mechanism of Autoxidative Degradation of Cellulose*, Restaurator 18:4, 1997, 163-176.
[25] The computer program STATGRAPHICS PLUS for Windows (version 2.1) was used for the extraction of the Principal Components. The same program was used for the calculation of the correlation coefficient.
[26] Bolch, B. W. and Huang, C., J., *Multivariate statistical Methods for Business and Economics*, Prentice – Hall, Englewood Cliffs, New Jersey, 1974.
[27] Moropoulou, A., Theoulakis, P., Chrysophakis, T., *Correlation between stone weathering and environmental factors in marine atmosphere*, J. Atmospheric Environment, 29, No 8 (1995) pp.895-903.
[28] Moropoulou, A., Bisbikou, K., Van Grieken, R., Torfs, K , *Correlation between aerosols, deposits and weathering crusts on ancient marbles,* J. Environmental Technology, 22 (2001), in press.
[29] The formula: $\Delta E = \left(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\right)^{1/2}$ was used. ΔE: total color difference, ΔL*: difference in lightness, Δα*: difference in the red – green axis and Δb*: difference in the yellow – blue axis (of the CIEL*α*b* color system) between the treated and the untreated sample. (see ASTM STANDARD D 2244 – 93: Standard Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates, 1993)
[30] Schaeffer T., Blyth-Hill V., Druzik J., Aqueous Light Bleaching of Modern Rag Paper: An Effective Tool for Stain Removal, The Paper Conservator, 21, 1997, p. 5.
[31] A. - L., Dupont, *Degradation of Cellulose at the Wet/dry Interface, II. An Approach to the Identification of the Oxidation Compounds*, Restaurator, 17:3, 1996, 145-164.
[32] Lienardy, Anne, Van Damme, Philippe, op. cit.
[33] Bansa, Helmut, op. cit.
[34] Solubility of $Ca(OH)_2$ in 20 °C: 1,63 g/l. Solubility of $Ca(HCO_3)_2$ in 20 °C: 3,8 g/l.