

INFLUENCE OF GALL INK COMPOSITION ON THERMAL STABILITY OF PAPER

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The study evidences the effects of gall ink ingredients on the thermal stability of paper by thermogravimetry and differential thermal analysis. Paper samples treated with different gall inks, as well as untreated paper and powdered Arabic gum, were subjected to thermal ageing. The thermal degradation of the samples was examined both before and after accelerated ageing, and the results obtained confirmed the variation of the parameters assessing the thermal stability of paper.

Keywords: gall inks, paper, thermal stability, thermogravimetry

INTRODUCTION

Thermogravimetry is an analytical technique commonly used to investigate cellulose materials. The dynamic techniques permit to reveal the reaction pathways in thermal degradation, thus providing a method for estimating the thermal stability of paper on the basis of kinetic parameters, during decomposition.

Numerous studies devoted to the thermal degradation of cellulose – the main component of paper – evidence the practical interest that it presents for different fields.¹⁻²⁷ Many researchers followed the catalytic action of metallic ions in thermo-chemical processes, as well as the impact of inorganic salts on the formation and distribution of cellulose pyrolysis products.²⁸⁻³⁰

In the heritage conservation field, thermal analysis has often offered additional data for a thorough characterisation of inorganic materials and organic binders, being also selected to estimate the weathering extent of natural fibres in ancient fabrics, since fibres undergo characteristic patterns of thermal degradation.³⁻³³

The application of thermogravimetry to determine the deterioration history of objects in archives or museums³⁴ was extended to studies on the methods of ancient paper manufacture.³⁵ It is also sometimes used in an attempt to predict any changes that would occur during restoration and conservation treatments.^{36,37}

The assessment of the general conditions for paper artefacts requires an extensive survey on the behaviour of cellulose under the impact of all factors that generate its deterioration.³⁸ Although thermal analysis is considered a convenient method for characterising heterogeneous organic materials, its micro-destructive nature requires that the studies on cultural heritage objects should be carried out on models. Working on models guarantees a reproducible background and allows the correlation of the natural weathering of real cellulose-based materials with the degradation degree of the aged samples.³⁹⁻⁴¹

Taking all these into consideration, the present work examines the influence of gall

ink ingredients on the thermal stability of paper, using model papers treated by gall inks. The ink solutions were prepared according to Romanian recipes widely used until the 20th century.

EXPERIMENTAL

Materials

The experiments were carried out on paper⁴² made from cotton linters submitted to alkaline delignification, un-sized, containing no fillers, weighing 25 g/m². The samples, designated as

C1...C6, were prepared by the manual application of six different ink solutions. The composition of the inks is given in Table 1.

For better evidencing the changes occurring in the thermal behaviour of paper cellulose, as due to ink composition, the ink preparation procedure involved a variation in ingredients.⁴³⁻⁴⁶ Ink solution number 5 eliminates a basic compound in colour formation, namely the soluble metal salt, while the binder (Arabic gum) is omitted in ink recipe 6.

Table 1
Ink composition

Solution ingredients	Ink solutions					
	1	2	3	4	5	6
FeSO ₄ ·7H ₂ O (mol·l ⁻¹)	0.507	0.057	0.190	-	-	0.086
Fe ²⁺ /GA* (mol·mol ⁻¹)	2.164	0.357	0.965	-	-	0.09
CuSO ₄ ·5H ₂ O (mol·l ⁻¹)	-	0.048	-	0.086	-	-
Cu ²⁺ /GA* (mol·mol ⁻¹)	-	0.302	-	0.402	-	-
Gallic acid (mol·L ⁻¹) (GA)	0.251	0.159	0.197	0.215	0.231	0.950
Arabic Gum (g·L ⁻¹) (AG)	98.2	55.9	18.0	52.9	26.1	-
pH	2.45	2.11	2.51	2.81	4.26	1.98

* The content of gallic acid (GA), after hydrolysis of tannins

Methods

Accelerated ageing

The reference paper (M), the papers containing gall ink solutions (C1÷C6) and the powdered Arabic gum (GA) were submitted to thermal ageing conditions, at 105 °C, according to ISO-5630-1991/ASTM-D776-87 standards.

Thermogravimetry

Thermogravimetric analysis was carried out on a Mettler Toledo instrument, in nitrogen atmosphere, using a steady flow of 20 mL·min⁻¹, at a heating rate of 15 °C per min, over a temperature range of 25÷600 °C.

The TGA dynamic curves, as well as the DTG curves, recorded for all samples have been analysed, both before and after accelerated ageing, as to the importance of ink composition in the pyrolysis process.

RESULTS AND DISCUSSION

Tables 2 to 9 list the experimental data on thermal degradation: T_i – initial temperature of mass loss, T_{max} – temperature at which the reaction rate reaches its maximum value, T_f – final temperature and W – mass loss.

The data from the thermograms recorded for the aged samples were also used to estimate the thermal stability of paper by the kinetic parameters of the thermal decomposition reaction. The difference-differential model developed by Freeman-Carroll⁴⁷ was employed for the determination of the kinetic triplet: activation energy (E_a), pre-exponential factor (lnk₀) and reaction order (n). In this model-fitting method, the kinetic equation for cellulose pyrolysis is given by

$$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)} = n - \frac{E_a}{R} \times \frac{\Delta \left(\frac{1}{T}\right)}{\Delta \ln(1-\alpha)} \quad (1)$$

where:

E_a – apparent activation energy, kJ·mol⁻¹;

n – reaction order;

dα/dT – reaction progress with temperature, mg·°C⁻¹;

α – conversion degree;

R – gas constant, J·mol⁻¹·K⁻¹; R = 8.3145 J·mol⁻¹·K⁻¹;

T – temperature, °C

Table 2
Thermogravimetric data for sample series C1, C3 and C6

Sample series	Ageing time (h)	Thermal degradation steps	T _i (°C)	T _{max} (°C)	T _f (°C)	W (%)
C1	0	I	263	297	406	68.92
	24	I	256	290	310	47.18
		II	310	371	458	23.11
	48	I	252	289	308	43.70
		II	308	364	455	22.67
	72	I	255	289	308	43.66
II		308	364	456	22.59	
C3	0	I	270	301	401	73.08
	24	I	273	301	398	72.77
	48	I	274	300	397	78.74
	72	I	273	303	411	72.76
C6	0	I	259	290	315	46.58
		II	315	370	408	24.58
	24	I	258	292	315	46.90
		II	315	375	436	25.55
	48	I	258	291	313	44.92
		II	313	374	430	22.30
	72	I	249	292	319	45.53
		II	319	374	466	22.32

T_i – initial temperature of mass loss; T_{max} – temperature of maximum reaction rate; T_f – final temperature; W – mass loss

Table 3
Kinetic parameters of the pyrolysis reaction for samples C1, C3 and C6

Sample series	Ageing time (h)	Thermal degradation steps	Ea (kJ·mol ⁻¹)	n	lnk ₀
C1	0	I	204.95±0.66	1.39±0.066	39.19±0.14
	24	I	199.61±0.85	1.21±0.084	38.53±0.22
		II	83.10±2.97	1.94±0.048	10.48±0.58
	48	I	195.74±0.85	1.14±0.0848	37.71±0.19
		II	72.03±4.68	1.97±0.085	8.22±0.92
	72	I	198.84±0.78	1.24±0.0809	38.37±0.17
II		64.89±3.04	1.55±0.0456	6.86±0.59	
C3	0	I	242.94±1.21	2.38±0.01276	47.14±0.26
	24	I	209.24±0.37	1.7±0.038	39.86±0.085
	48	I	236.25±0.67	1.96±0.0673	45.75±0.15
	72	I	246.53±0.77	2.74±0.0867	47.71±0.17
C6	0	I	172.90±0.62	1.36±0.0731	32.69±0.14
		II	71.78±2.32	1.83±0.03932	8.39±0.46
	24	I	180.17±0.57	1.48±0.0664	34.17±0.13
		II	65.51±2.13	1.72±0.03427	7.12±0.42
	48	I	173.86±0.49	1.28±0.0558	32.83±0.11
		II	85.72±2.94	2.33±0.0557	11.09±0.58
	72	I	183.27±0.50	1.47±0.0539	34.85±0.11
		II	61.44±2.39	1.59±0.03898	6.34±0.47

Ea – activation energy; n – reaction order; lnk₀ – pre-exponential factor

Table 4

Thermogravimetric data for sample C4

Ageing time (h)	Thermal degradation steps	T _i (°C)	T _{max} (°C)	T _f (°C)	Mass loss W (%)
0	I	269	339	377	77.70
24	I	278	343	376	78.89
48	I	269	333	370	76.41
72	I	285	340	373	79.34

Table 5
Pyrolysis kinetic parameters for the thermal degradation of sample series C4

Ageing time (h)	Thermal degradation steps	Ea (kJ·mol ⁻¹)	n	lnk ₀
0	I	58.62±0.35	0.69±0.0632	6.22±0.075
24	I	75.97±0.26	0.76±0.0465	9.72±0.0548
48	I	40.57±0.47	0.52±0.0850	2.56±0.10
72	I	84.97±0.31	0.91±0.0505	11.71±0.066

Table 6
Thermogravimetric data for samples C2 and C5

Sample series	Ageing time (h)	Thermal degradation steps	T _i (°C)	T _{max} (°C)	T _f (°C)	Mass loss W (%)
C2	0	I	307	348	371	76.18
	24	I	272	299	406	74.20
	48	I	275	308	379	80.48
	72	I	283	326	377	76.94
C5	0	I	330	365	388	80.97
	24	I	330	365	387	81.38
	48	I	330	365	387	80.42
	72	I	324	362	384	79.43

Table 7
Kinetic data for the thermal degradation of sample series C2 and C5

Sample series	Ageing time (h)	Thermal degradation steps	Ea (kJ·mol ⁻¹)	n	lnk ₀
C2	0	I	178.71±0.56	1.16±0.059	30.30±0.11
	24	I	156.62±2.61	2.63±0.0393	28.15±0.56
	48	I	125.32±2.09	2.08±0.0322	21.04±2.09
	72	I	99.42±1.17	1.35±0.0174	15.03±0.25
C5	0	I	177.45±0.19	0.90±0.0196	28.89±0.0376
	24	I	175.98±0.15	0.83±0.0155	28.62±0.03036
	48	I	174.95±0.32	0.85±0.0349	28.43±0.0637
	72	I	171.94±0.18	0.88±0.0193	28.02±0.0358

Table 8
Thermogravimetric data for unaged paper samples and unaged Arabic gum

Sample	Thermal degradation steps	T _i (°C)	T _{max} (°C)	T _f (°C)	Mass loss W (%)
M	I	313	361	377	99.89
C5	I	330	365	388	80.97
C1	I	263	297	406	68.92
C4	I	269	339	377	77.70
AG	I	283	313	333	70.10

Table 9
Values of pyrolysis kinetic parameters for the unaged samples M, C1, C4, C5 and AG

Sample	Thermal degradation steps	E _a (kJ·mol ⁻¹)	n	lnk ₀
M	I	143.64±1.07	0.48±0.0112	22.52±0.21
C1	I	204.95±0.66	1.39±0.066	39.19±0.14
C4	I	58.62±0.35	0.69±0.0632	6.22±0.075
C5	I	177.45±0.19	0.90±0.0196	28.89±0.0376
AG	I	117.92±1.21	0.86±0.0198	19.42±0.27

Influences of Fe²⁺/GA molar ratio

The data recorded for sample series C1, C3 and C6, containing FeSO₄·7H₂O, are summarized in Table 2.

The results for the C1 series, given in Table 2, indicate that the paper was thermally degraded in one step, in the unaged sample, and in two steps in the samples aged for 24, 48 and 72 h. At the same time, a comparison between the values of the initial temperature (T_i) of thermal degradation showed a thermal stability reduction with (7÷11) °C. The same conclusion can be drawn when comparing the temperature whereby the reaction rate reaches its maximum (T_{max}). For the thermally degraded samples, the values recorded were around 289 °C. The second step begins at temperatures higher than 308 °C and the mass loss is of about 23%.

Thermogravimetric results for sample series C6 revealed a two-step thermal degradation process, resulting in a comparable mass loss percentage. No significant variations were recorded in the first step for the values of temperatures T_i and T_{max}; the second step begins at values over 308 °C.

The paper samples from the C3 series are thermally degraded in a single step.

From the results listed above for sample series C1, C3 and C6, it can be concluded that an increase in thermostability is gained

in the C3 series, consisting of samples treated with lower amounts of FeSO₄·7H₂O than those from the C1 series.

Taking into account the initial temperature of the mass loss T_i, the thermostability of both the C1 and C6 series is practically the same. Similar conclusions can be formulated when considering the values of temperature at which the reaction rate reaches its maximum in the first degradation step.

Table 3 describes the kinetic parameters derived from the Freeman-Carroll method for the C1, C3 and C6 series. The calculated values confirm the decreasing thermal stability of aged samples treated with gall inks weigh as compared to the unaged ones. It was noticed that, in the second degradation step, E_a decreases with the paper oxidation degree from 83 to 64 kJ/mol.

The calculation of the activation energy gave higher values for the C3 series of papers (in which the Fe²⁺/GA ratio is of 0.96) compared to the values from the C1 series (with a Fe²⁺/GA ratio equal to 2.164) and the C6 series (with Fe²⁺/GA = 0.09, and no Arabic gum), thus confirming a better thermal stability for the C3 samples.

The effect of metal ions

Samples C4 were obtained by replacing the iron salt with the copper salt in the ink recipe, which permitted to compare the

effects of both iron and copper ions on paper thermal stability. The main thermal characteristics established in this case are shown in Table 4.

It can be easily observed from Table 4 that the C4 samples show a better behaviour, from the viewpoint of thermal stability, than the C1 sample series. This is evident when considering not only the temperature at which thermal decomposition started, but also, and most importantly, the maximum values reached during pyrolysis. During the process, the C4 series presented a shift of T_{max} values to temperatures about 30-40 °C higher than that observed for the iron-containing samples C1, C3 and C6, while increasing the duration of ageing. For papers C4, the kinetic parameters of thermal decomposition presented the results listed in Table 5.

The estimated activation energy (Table 5) takes obviously lower values, which indicates a different pattern in the thermal degradation reaction for the copper gall ink treated paper.

The influence of inorganic salts

To assess the influence of some inorganic compounds on the thermal stability of paper, a comparison has been made between the C2 series, consisting of papers containing both iron and copper salts, and the paper containing none of these salts, from series C5.

The thermogravimetric characteristics are presented in Table 6, while Table 7 contains the calculated values of the activation energy

E_a , the pre-exponential factor $\ln k_0$ and the reaction order.

For the activation energy, the results shown in Table 7 display a linear correlation with the time of the thermal ageing treatment, at a slower rate in the case of samples C5.

Considering the values for the initial temperature of thermal degradation T_i in terms of accelerated ageing progress with time, for the paper samples denoted as C1, C2, C4 and C5, the following series of thermal stability may be established:

$C1 < C4 < C2 < C5$, for unaged samples;

$C1 < C2 \approx C4 < C5$, after 24 h of ageing treatment;

$C1 < C4 = C2 < C5$, after 48 h of ageing treatment and

$C1 < C4 = C2 < C5$, after 72 h of ageing treatment.

Consistent with the observed effect in the thermal degradation of paper, this resulting succession agrees with the studies highlighting the role of inorganic salts in decreasing thermal stability.

The overall influence of ink composition

The thermogravimetric data recorded in Table 8, the DTG curves from Figure 1 and the values of the thermal degradation kinetic parameters listed in Table 9 describe the unaged samples of reference paper (M), papers containing an iron ink solution (C1), papers containing a copper ink solution (C4) and papers containing a solution of Arabic gum and gallic acid (C5).

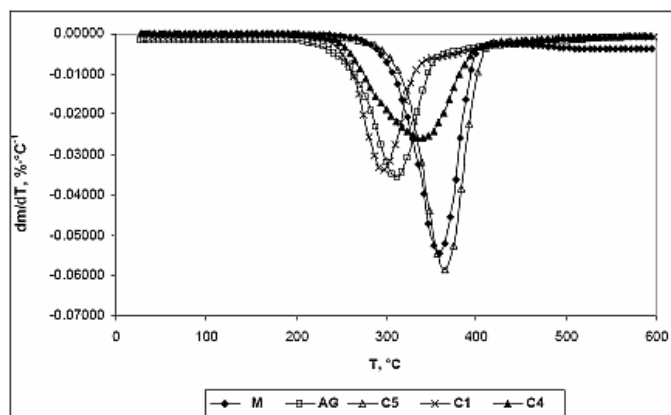


Figure 1: DTG curves for unaged samples M, C1, C4, C5 and AG

This selection of data allows a comparison likely to reflect the characteristics of the thermal decomposition reaction of paper as related to ink composition.

As seen from Figure 1 and Table 8, almost the same values of the temperature of maximum reaction rate are attained for both reference paper M and papers in the C5 series – treated with solutions containing no metal salts. The lowest values are recorded for the C1 samples treated with an iron gall ink solution. The values of T_{\max} for the papers treated with copper gall inks (C4 samples) are about 10 ± 15 °C lower than those for the paper series M and C5.

CONCLUSIONS

- The present study evidences an obviously decreasing tendency in the thermal stability of papers treated with ink solutions, recorded for aged *versus* the unaged paper samples.
- The presence of additives, namely iron and copper inorganic salts, in inks, along with the organic binder (usually, Arabic gum) has been shown to influence paper thermal stability.
- The metallic ions present in gall ink composition are acting as catalysts in cellulose oxidation processes and exert a major influence on the thermal stability of treated paper.

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