Journal of Thermal Analysis, Vol. 33 (1988) 1153–1157

INVESTIGATION OF PAPER SAMPLES BY EGA

F. Hevesi Tóth[1], *G. Pokol*[2], *J. Györe*[1] and *S. Gál*[2]

[1] MINISTRY OF THE INTERIOR, P.O.B. 314/32, BUDAPEST 1903, HUNGARY
[2] INSTITUTE FOR GENERAL AND ANALYTICAL CHEMISTRY, TECHNICAL UNIVERSITY OF BUDAPEST 1521, HUNGARY

An EGA method measuring the vapours and gases containing organic carbon was applied to study paper ageing. In a DuPont 916 Thermal Evolution Analyzer the original and aged paper samples were heated in a temperature programmed furnace, and the evolving volatiles are swept by an inert gas into a hydrogen flame ionization detector.

The low temperature section of the EGA curves (before the main decomposition step) is sensitive to the slight changes caused by ageing. In the case of naturally aged papers (stored at room temperature), the older the samples of the same quality were, the more intensive was the evolution of organic substances at temperatures below 250 °C. The differences among samples subjected to accelerated (thermal) ageing were an order of magnitude smaller. This points to the differences between the processes of natural and thermal againg.

Research work concerned with the processes of paper ageing and the possibilities of diminishing its effects have several goals: describing the causes of deterioration during storage, developing procedures for conservation and working out permanent paper qualities. A part of the studies is related to forensic problems, such as identification of documents, determination of their origin and the estimation of their age. Our studies on cellulose and paper ageing [1–3] also belong to this field.

In the present work, we used an evolved gas analysis technique measuring the organic gases and vapours leaving the sample during programmed heating. This method had not been applied in paper ageing studies before.

Experimental

Measurements were carried out on a DuPont 916 Thermal Evolution Analyzer [4] and 951 Thermogravimetric Analyzer. Characteristic ratios were used in the comparison of the EGA curves belonging to the same quality but different ages: $\alpha(250°)$, the ratio of the partial area under the EGA curve to 250° and the total area; $S(\text{Max})/m$, the signal intensity at the peak maximum related to the sample mass; and $S(250°)/S(\text{Max})$, being the ratio of the signal intensities at 250° and at the maximum, respectively.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

The paper samples were of well defined composition [5]. Series FT consisted of commercial writing and printing papers of different ages, stored under identical circumstances. The same paper qualities were thermally aged at 100° and 50% R.H. for 2–120 h, and the resulting samples constituted series FM.

Results and discussion

Figure 1 presents the TG, DTG and EGA curves of FT–3(1958). The mass loss to about 100° is due to the adsorbed water. The oxidative decomposition started above 250°, and consisted of two parts. Above 500°, the mass became constant, the residue being the ash content originating mainly from the loading agent. The EGA curve (recorded in inert atmosphere) shows but one decomposition peak with a shoulder near 200° followed by a slowly rising part (formation of organic decomposition products).

In the following, the results of FT-3 samples of different ages are discussed. The low temperature region of the EGA curves (Fig. 2) was found to be

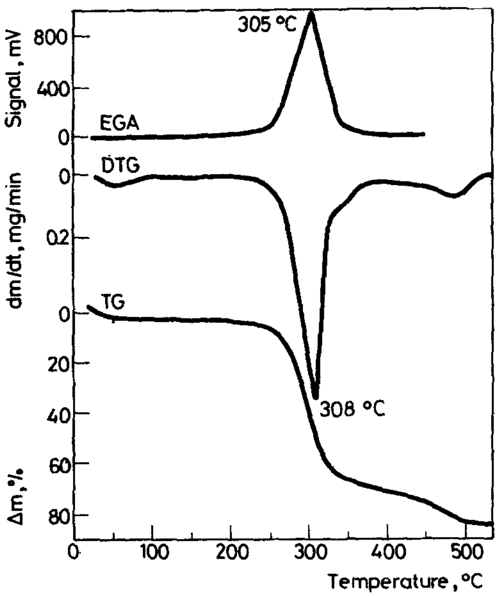

Fig. 1 Thermoanalytical curves of paper FT-3 (1958). The TG and DTG curves of a 3.48 mg sample were recorded in flowing air, with a heating rate of 10 deg min^{-1}. EGA: a 2.83 mg sample was run in nitrogen with 8 deg min^{-1}.

related to the age. For older papers the starting temperature of the evolution of organic substances is lower, and the part of the EGA curve below 250° is higher. This points to the fact that, during a long storage, volatile organic decomposition products are formed. This phenomenon was common for all the investigated papers aged naturally (i.e., stored in normal conditions). The behaviour of the paper manufactured in 1978 was different from the others, which may probably be explained by some discrepancy in the composition and technology.

The parameters characterizing the EGA curves (mentioned above) are plotted in Fig. 3 as a function of the year of manufacture. The $\alpha(250°)$ and the $S(250°)/S(\mathrm{Max})$ values show an increasing trend with the age, while $S(\mathrm{Max})/m$ changes in the opposite direction.

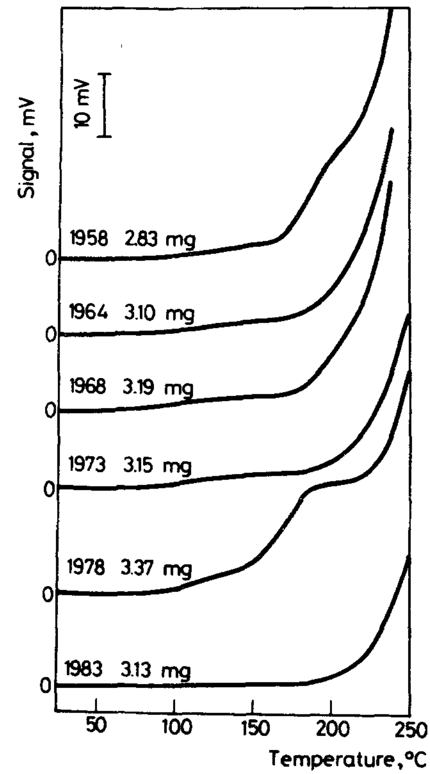

Fig. 2 The low temperature section of the EGA curves of papers FT-3 manufactured in different years, after natural ageing.

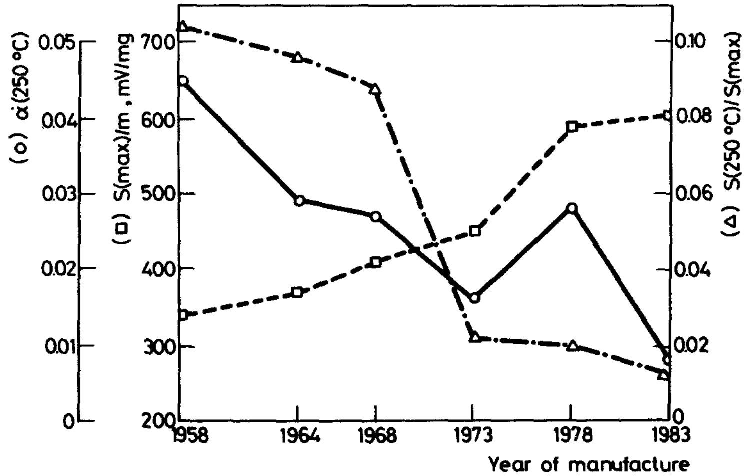

Fig. 3 Characteristics of the EGA curves of papers FT-3 manufactured in different years, after natural ageing

Evolution of organic substances was also observed in the low temperature part of the EGA curves of thermally aged samples. However, the values of $\alpha(250^{\circ})$, $S(250^{\circ})/S(\mathrm{Max})$ are an order of magnitude lower than those of naturally aged papers, the changes of the parameters are very small and poorly reproducible. During the accelerated ageing, presumably, the majority of the volatile products leave the sample, which may explain this behaviour.

Conclusion

The EGA curves of papers subjected to natural ageing show the increase of the amount of organic decomposition products formed during storage, and thus the method is suitable for the investigation of ageing processes. The changes in the low temperature section of the EGA curves were found an order of magnitude smaller for thermally aged samples than in the case of naturally aged ones. Therefore, EGA offers a possibility to distinguish the effect of natural and accelerated (thermal) ageing, which is important from the aspect of forensic investigations.

References

1 F. Hevesi Tóth, G. Pokol, É. Buzágh-Gere, J. Györe and S. Gál, Cellulose Chem. Technol., 18 (1984) 99.
2 F. Hevesi Tóth, G. Pokol, J. Györe and S. Gál, Thermochim. Acta, 80 (1984) 251.
3 F. Hevesi Tóth, G. Pokol, J. Györe and S. Gál, Thermochimica Acta, 93 (1985) 405.
4 F. T. Eggertsen, E. E. Seibert and F. H. Stross, Anal. Chem., 41 (1969) 1175.
5 F. Hevesi Tóth, Studies on Paper Ageing, Especially by Means of Thermal Methods, C. Sc. Thesis, Budapest 1986, p. 25 (in Hungarian).

Zusammenfassung – Eine EGA-Methode zur Messung von kohlenstoffhaltigen Gasen und Dämpfen wurde zur Untersuchung der Alterung von Papier verwendet. In einem DuPont 916 Thermal Evolution Analyzer werden frische oder gealterte Papierproben in einem temperaturprogrammierten Ofen aufgeheizt und die entweichenden flüchtigen Produkte mit einem Inertgasstrom einem Wasserstoff-Flammenionisationsdetektor zugeführt.

In ihrem Tieftemperaturbereich vor der Hauptzersetzung spricht die EGA-Kurve empfindlich auf die geringen Änderungen infolge der Alterung an. Bei natürlich (d.h. bei Raumtemperatur) gealterten Papieren gleicher Qualität wird mit steigendem Alter eine zunehmende Freisetzung organischer Produkte unterhalb 250 °C gefunden. Die Unterschiede zwischen Papieren nach beschleunigter Alterung (bei erhöhter Temperatur) sind um eine Größenordnung geringer. Das deutet auf Unterschiede der Prozesse der natürlichen und künstlichen Alterung.

РЕЗЮМЕ — Для исследования процессов старения бумаги был использован метод АВГ, позволяющий проводить измерения паров и газов, содержащих органический углерод. Исходные и старые образцы бумаги подвергались программированному нагреву в термоанализаторе Дюпон 916, а выделяющиеся при этом летучие продукты переносились инертным газом в водородный пламенно-ионизационный детектор. Низкотемпературный участок кривых АВГ (перед стадией основного разложения) является чувствительным к тем незначительным изменениям, вызванных процессом старения. В случае более старых образцов бумаги, подвергшихся старению в естественных условиях (при комнатной температуре), выделение органических веществ происходило более интенсивно при температурах ниже 250°. Среди образцов бумаги, подвергнутых ускоренному (термическому) старению, различия были на порядок меньше. Это основные критерии различия между процессами естественного и ускоренного (термического) старения бумаги.