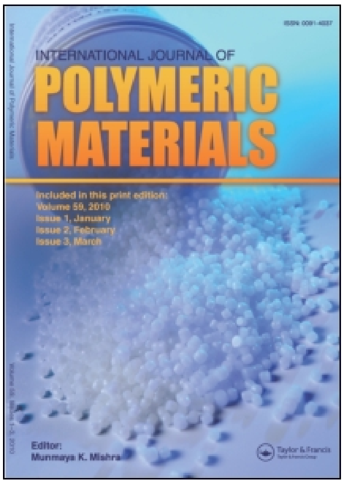


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Novel Beater Additives for Paper

Altaf H. Basta[a]; Houssni El-saied[a]
[a] Cellulose and Paper Dept., National Research Centre, Cairo, Egypt

To cite this Article Basta, Altaf H. and El-saied, Houssni(2001) 'Novel Beater Additives for Paper', International Journal of Polymeric Materials, 50: 2, 185 — 205
To link to this Article: DOI: 10.1080/00914030108035100
URL: http://dx.doi.org/10.1080/00914030108035100

Intern. J. Polymeric Mater., 2001, Vol. 50, pp. 185–205
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.

Novel Beater Additives for Paper

ALTAF H. BASTA and HOUSSNI EL-SAIED*

Cellulose and Paper Dept., National Research Centre,
Dokki-12622, Cairo, Egypt

(Received 26 August 1999)

Novel beater additives were prepared and the properties of the produced paper sheets were studied. From the results of non-isothermal thermogravimetric analysis of the prepared paper sheets, these additives can be used as a fire retardant.

The results obtained also show that, this type of additives is suitable for producing magnetic paper, whereas its mass succeptibility value in some time is greater than that produced from adding magnetic metal oxides under the same conditions of preparation; while its semiconductor property is relatively higher than that obtained from adding metal oxides.

In addition, using of such additives accept the sheets high strength properties, porous structure (air permeability value ~ 800 ml/min.), and water resistance behavior. Its resistivity to water absorption is better than that obtained by chemically modification of the pulp to decrease its hydrophilicity, *e.g.*, acetylation and grafting by hydrophobic monomer. Therefore, this type of paper sheets is suitable as a Nursery-plant boats.

The biological evaluation of the produced paper sheets reveals that, the addition of novel additives gains the paper some anti-microbial action.

Keywords: Paper; Additives; Flame retardancy

INTRODUCTION

The flame retardancy and magnetic properties are an added value to the traditional characteristics of paper, in an attempt to control smoke generation and toxicity, and gain it a magnetic recording (magnetographic printing), information storage and security media, as well as electromagnetic shielding.

---

*Corresponding author.

For flaming combustion of cellulosic materials a depolymerization of cellulose into levoglucosans [1,6-anhydro-β-D-glycopyranose] is regarded as the main formation of the fuel for the flame. The main theory of flame retardant is to minimize the formation of levoglucosan by lowering the decomposition temperature of cellulose and enhancing char formation by catalyzing the dehydration and decomposition reactions [1–3]. The literature reveal that, the flame retardancy is resulted from the presence of some elements such as phosphorous, halogens, nitrogen or boron in the retardant [4, 5]. Phosphorous compounds strongly affect pyrolysis and char formation, whereas the halogens considerably influence polymer breakdown and combustion. Nitrogen in combination with phosphorus has a synergistic effect. Phosphoric acid and aluminum chloride probably increased the rate of dehydration; while boric acid may have inhibited levoglucosan formation. Dehydration reactions of polysaccharides, catalyzed by many inorganic salts, lead to a higher portion of charing with a reduced amount of evolved glycosans.

For magnetic paper, the maghemite (γ-Fe_2O_3) and magnetite Fe_3O_4 are the most widely used magnetic pigments in the production of magnetic recording and information storage media. A common application for maghemite is the encoding of information on subway tickets in the form of a thin magnetic strip coated on the cardboard stock [6]. Magnetic fibers are also obtained by synthesizing ferrites *in-situ* using suitable natural cellulose fibers possessing appropriate functional groups or chemically modified cellulose fibers to introduce these functional groups, *e.g.*, carboxyl, sulphonyl and sulphate groups [7–9].

In this study, hydroxyethyl cellulose-Fe(III)[HEC-Fe(III)], carboxymethyl cellulose-Fe(III)[CMC-Fe(III)] and carboxymethyl cellulose-Zn(II)[CMC-Zn(II)] complexes were prepared and used as beater additives during the formation of paper sheets from wood pulp. The thermal degradation, magnetic, electrical conductivity and strength properties of the prepared sheets, in comparison with those prepared from adding CMC and metal oxides (Fe_2O_3 and ZnO) were studied. The application of using the paper sheets including cellulose ether metal complexes as Nursery-plant boats was also studied.

EXPERIMENTAL

Materials and Handsheets Paper Making

- Paper grade kraft soft wood pulp, as a paper substrate, was delivered from Rakta Paper Mill, Alexandria, Egypt. The pulp was chemically analysed as α-cellulose [10], pentosans [11], lignin [12] and ash.
- Complexes of cellulose ethers (hydroxyethyl cellulose and carboxymethyl cellulose) with analytical reagent grades of $FeCl_3$ and Carboxymethyl cellulose with analytical grades of $Fe(NO_3)_3$, $ZnCl_2$, Fe_2O_3 and ZnO were prepared and used as a beater additives. The hydroxyethyl cellulose (HEC) and carboxymethyl cellulose (CMC) used as a type of cellulose ether (ligands) were purchased from Fluka Chemical Co. The preparation of the cellulose ether complexes as the method described in our previous work [13].
- Based on the amount of magnetic oxide conventionally added during the preparation of magnetic paper [14], and for the sake of comparison between the properties of paper made from using metal complexes with those made from adding metal oxides, 30% beater additives were used in this investigation Sheets paper samples were prepared as the method described elsewhere [15].

MEASUREMENTS

Thermal Analysis

Thermogravimetric analysis (TG and DTG) of the prepared paper sheets were done using PERKIN ELIMER (Thermogravimetric Analyzer TGA7). Analysis was performed with a heating rate 10°C/minute and nitrogen flow rate 50 cc/minute, under nonisothermal conditions.

Magnetic Measurement

Measurements of magnetic susceptibility (mass, c.g.s unit) were carried out using Gouy balance and $Hg[Co(SCN)_4]$ as calibrant.

Electrical Conductivity

The samples for AC (alternate current) electrical measurement were cut from the paper sheets, of thickness 1 mm, into disks of 2.3 cm in diameter, stacked between disk electrodes of 2.3 cm in diameter to form a cell. The AC conductiviy was measured by using a cell Cu/sample/Cu.

Strength Properties, Water Absorption and Air Permeability

Untreated, metal complexes and CMC-metal oxides containing paper sheets samples were conditioned at relative humidity 65% and temperature 20°C, then they were tested for breaking length, burst factor and tear factor [16]. Water absorption of paper was determined by immersing the sheet in water at 23°C for 24 hrs. The paper was then removed from water and placed between two plotting papers and a cylinder of 6 kg was passed on it for five times. The wet sheet was then quickly weighed, and then reweighted after its drying at 105°C. The permeability of paper sheets was measured according to Ref. [17].

Biological Evaluation

The antimicrobial actions of the paper samples on Bacillus stabtilis NRRL B-543, Escherichia colli NRRL b-210, Staphylococcus aureus, Pseudomonas aeruginosa, Aspergillus niger, Sacchoromyces Cervisiae, Salmonella typhi, Candida albicous, and Penicillum chrysogen were conducted using the technique of agar plate method [18].

Scanning Electron Microscope (SEM)

A scanning electron microscope Nanolab 7 produce by SEMCO Instrument Co. Ottawa-Canada, was used. The photographic conditions were kept constants all over the investigated paper samples. Acceleration voltage of electron beam 20 kv, the time taken for a photograph is 60 sec. Scanning electron microscopic structures were observed at magnfication of 250 and 500.

RESULTS AND DISCUSSION

Table I repesents the chemical constituents of the paper grade wood pulp and the strength properties and water absorption of handsheet made from it.

Thermal Analysis

The nonisothermal TG and DTG curves of paper sheets prepared from untreated, cellulose ether-metal complexes and CMC-metal oxides treated wood pulp are illustrated in Figures 1–3, while Figure 4 shows the variation of decomposition temperature (T_d) with the percentage of weight loss for examined paper sheets.

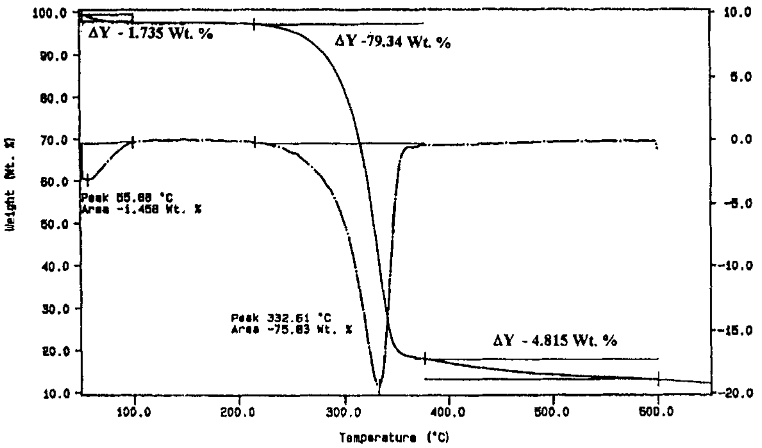
From Figures 1–3 it is clear that, in all paper samples, three degradation stages are observed. The first stage at temperature $\leq 100°C$, this is due to the loss of the sorbed moisture. While at temperature region 190–380°C, the degradation stage is due to the following reactions hydrolysis of glycosidic bonds (depolymerization), thermooxidation and dehydration (inter and intramolecular), this stage controls the formation of laevoglucosan, which regards as the main formation of the fuel for the flame [3]. At higher temperature ($> 331-380°C$) the degradation stage is due to the rapid volatilization accompanied by the formation of carbonaceous.

From Figure 4 it is clear that, the addition of oxides, especially Fe_2O_3 with CMC during beating stage improves the resistivity of wood pulp paper sheet to thermal decomposition, compared with beating addition of cellulose ether-Fe(III) complexes in wood pulp fibers. The

TABLE I Chemical analysis of wood pulp and strength properties and water absorption of obtained paper sheets

Measurement	*Value*
α-Cellulose, %	86.60
Pentosans, %	7.00
Lignin, %	Trace
Ash, %	0.19
Breaking length, m	4539.35
Burst factor	33.07
Tear factor	108.07
Water absorption, %	130.52

Wood Pulp



HEC-FeCl3 complex treated pulp

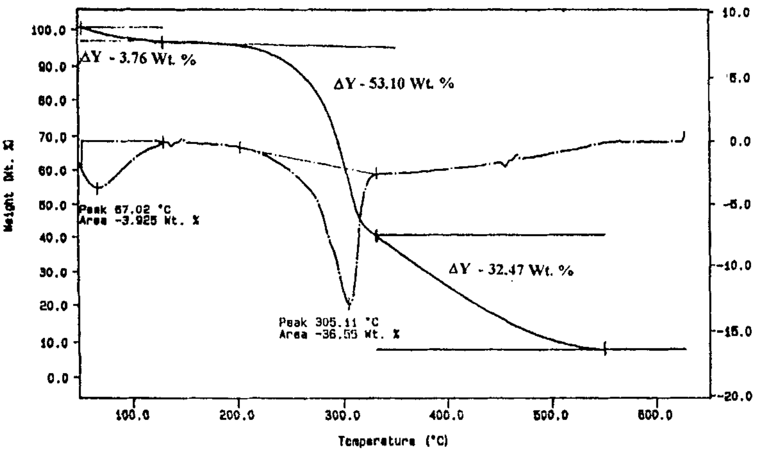


FIGURE 1 TGA and DTG thermograms of paper sheets prepared from untreated and HEC-Fe(III) complex treated wood pulp.

addition of cellulose ether-Fe(III) complex leads to shift the decomposition temperature, especially at 10%–40% weight loss, to a lower value, compared with untreated sheets. The extent of shift behaves the following order paper sheet including HEC-$FeCl_3$ complex > CMC-$FeCl_3$ > CMC-$Fe(NO_3)_3$ > CMC-$ZnCl_2$.

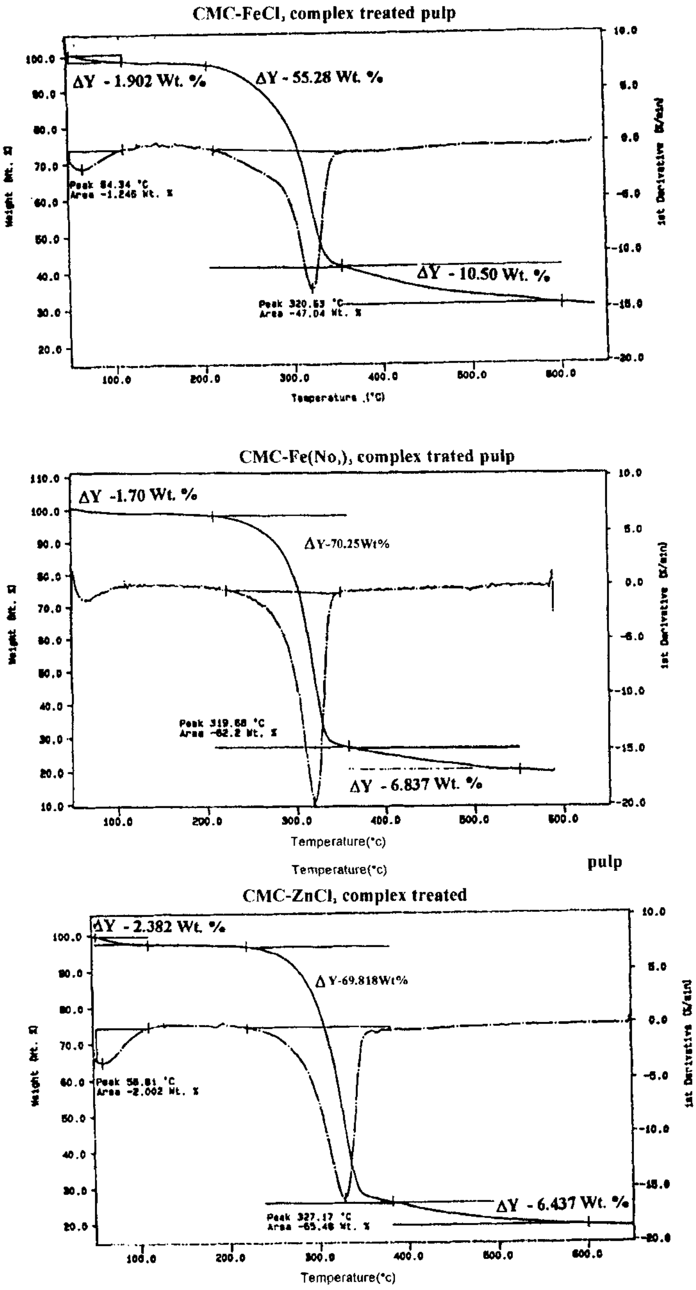
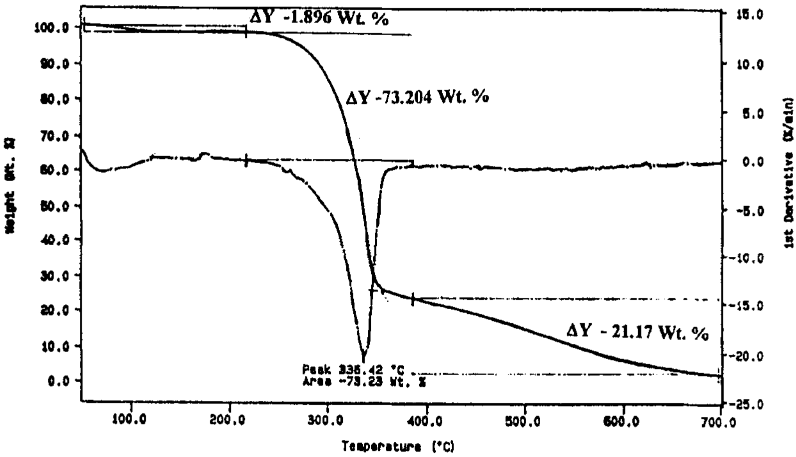


FIGURE 2 TGA and DTG thermograms of paper sheets prepared from CMC-metal complexes treated wood pulp.

CMC- Fe_2O_3 treated pulp



CMC-ZnO treated pulp

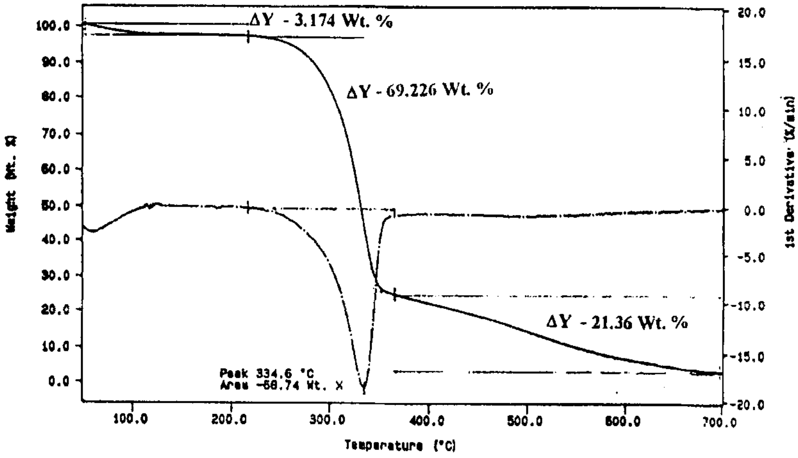


FIGURE 3 TGA and DTG thermograms of paper sheets prepared from CMC-metal oxides treated wood pulp.

Calculation of Arrhenius Parameters

The determination of Arrhenius parameters (activation energy, specific rate constant and Arrhenius factor), from weight loss *versus*

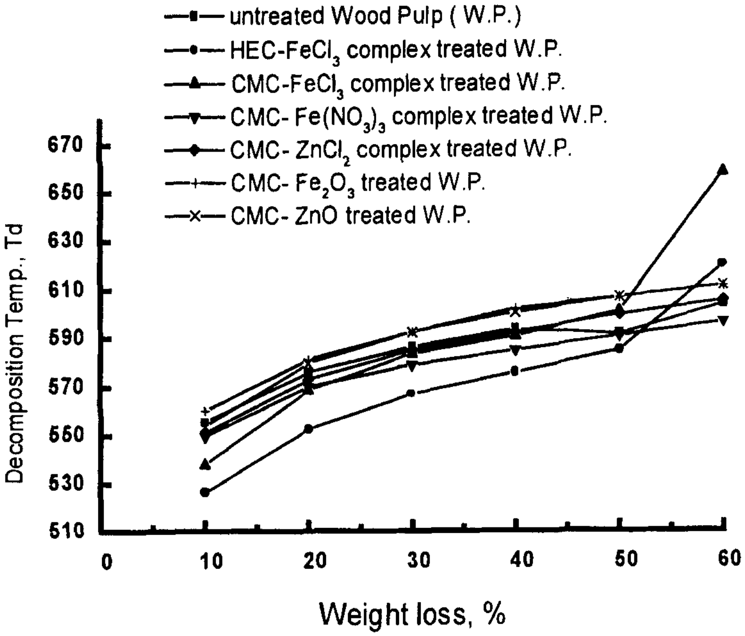


FIGURE 4 Temperature of decomposition, T_d, of untreated and wood pulp treated paper sheets, at different percentages of weight losses.

temperature data, can be carried out using Coats and Redfern equation [19];

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log_{10}\left[\frac{AR}{aE_a}\left(1-\frac{2RT}{E_a}\right)\right] - E_a/2.3\ RT$$

where (α) is fractional conversion, (n) is the order of degradation reaction, (a) is the heating rate (in k min^{-}), (R) is the gas constant (in kJ mol^{-1} K^{-1}), (T) is the temperature (in K), (A) is the frequency factor (s^{-1}), and (E_a) activation energy (kJ/mol).

Plotting the left-hand-side values of the equation, *i.e.*, $\log_{10}[(1-(1-\alpha)^{1-n}/T^2(1-n))]$ against ($1/T$) using various values of (n), should give a straight line with the most appropriate value of (n). Thus, the method of least square is applied for the equation, taking values of (n) ranging from zero to 3.0 with increment of 0.5, and calculating for each value of (n), the correlation coefficient ($-r$), standard error estimation (Se). The (*n*) values which corresponds to the maximum ($-r$), and minimum (Se) is the order of degradation process [20]. The activation energies and frequency factors were calculated from the slope and intercept, respectively, of the Coats and Redfern equation with the most appropriate value of (*n*).

Figures 5–7 show the plots of $-r$, Se and E_a as a function of "*n*", of the main degradation stages (depolymerization and dehydration stages) of all samples under examination. The Arrhenius parameters, order of thermal degradation are recorded in Table II. From this table it is clear that, the appropriate order of degradation stage of untreated paper sheet follows the 0.5 order; while for cellulose ether-metal complexes treated paper sheets follow the zero order. This indicates that the order of degradation reaction does not dependent on the type of cellulose ether-metal complexes; while the reverse is observed in the case of CMC-metal oxides treated paper sheets.

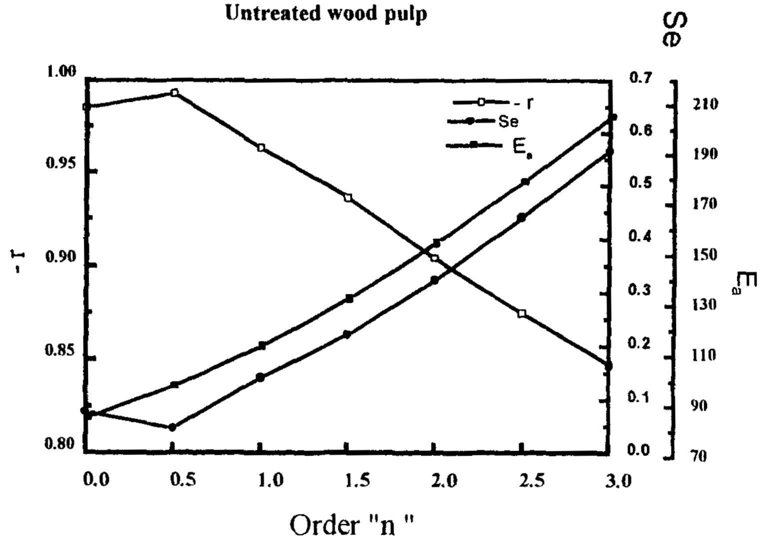
The values of DTG peaks and specific rate constant (Figs. 1–3 and Tab. II) show that, the using of cellulose ether-metal complexes as beater additive increased the rate of depolymerization and dehydration of the prepared paper samples, in addition to increase the percentage of the residue (*i.e.*, decreased the formation of laevoglucosan), compared with addition of CMC-metal oxides. The addition of cellulose ether-$FeCl_3$ complex gains the paper sheet a relatively high flameproofing than cellulose ether-$ZnCl_2$ complex. This may be related to the type of combination of metallic ions in complex formation. Whereas, the ionically bond is formed in the case of CMC-$ZnCl_2$ complex; while covalent coordinated bond is formed in the case of cellulose ether-$FeCl_3$ complex [21]. The former bond is more stronger than the latter bond. Therefore, this ionic bond decreases the rate of depolymerization and dehydration of cellulose samples.

It is clear that (Tab. II), the improving the fire retardancy of paper sheets as a result of adding complexes or oxides follows the sequence: HEC-$FeCl_3$ > CMC-$FeCl_3$ > CMC-$Fe(NO_3)_3$ > CMC-$ZnCl_2$ > CMC-ZnO > CMC-Fe_2O_3.

Magnetic and Electrical Properties

Table III shows the values of the mass succeptibility (x_g, c.g.s) and AC-conductivity (σ ohm^{-1} cm^{-1}) of paper samples under investigation.

Untreated wood pulp



HEC-FeCl$_2$ complex treated wood pulp

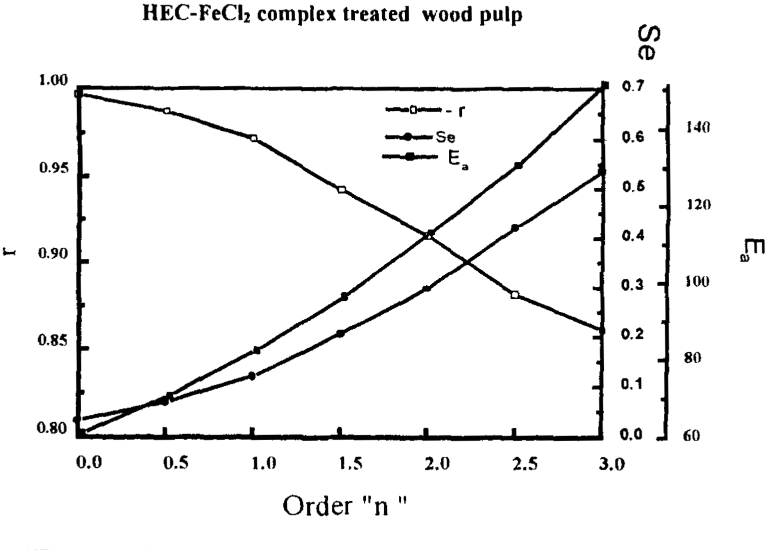
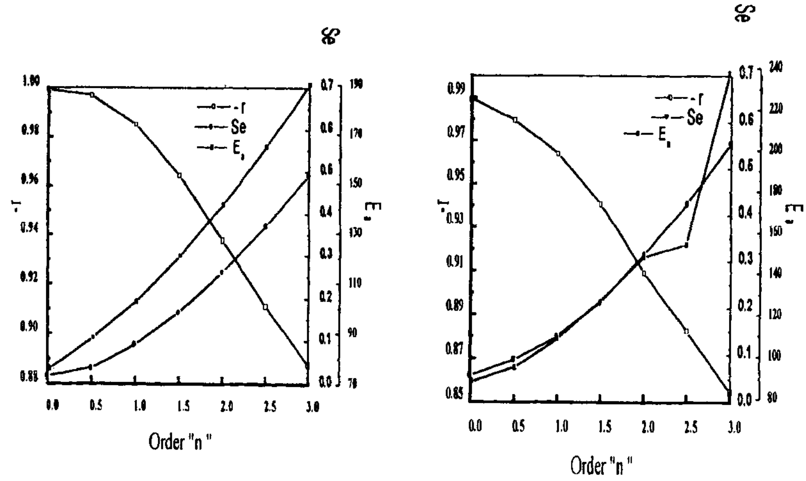
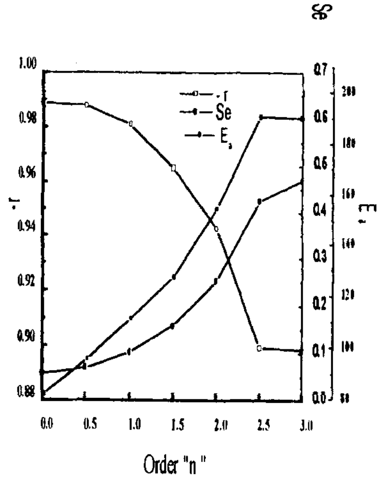


FIGURE 5 Statistical determination of "n" and "E_a" of the main thermal degradation stage of paper sheets prepared from untreated and HEC-FeCl$_2$ complex treated wood pulp.

The x_g and σ the paper sheets made from adding magnetic and semiconductor oxides (Fe$_2$O$_3$ and ZnO) with CMC under the same conditions of preparation were also measured for comparison.



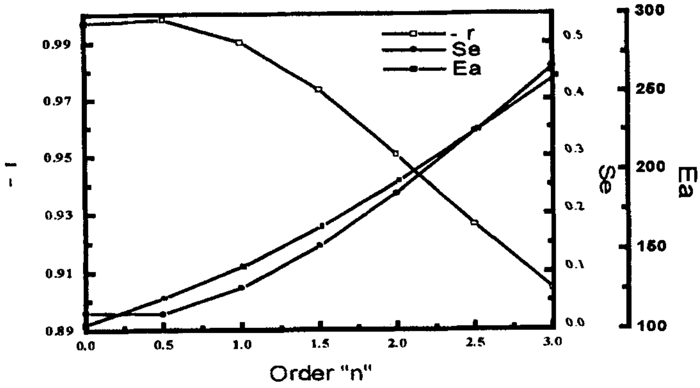
CMC- FeCl₃ complex treated wood pulp **CMC- ZnCl₂ complex treated wood pulp**



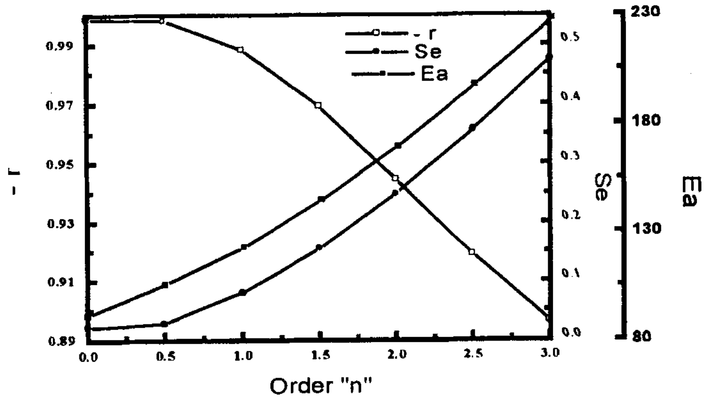
CMC- Fe(NO₃)₃ complex treated wood pulp

FIGURE 6 Statistical determination of "*n*" and "E_a" of the main thermal degradation stage of paper sheets prepared from CMC-metal complexes treated wood pulp.

It is clear that, CMC-Fe(III) complexes beater additives gain the paper sheets a relatively high x_g than HEC-Fe(III) and CMC-Zn(II) complexes. For the electrical conductivity property, Table III shows



CMC- Fe_2O_3 treated wood pulp



CMC- ZnO treated paper sheet

FIGURE 7 Statistical determination of "*n*" and "E_a" of the main thermal degradation stage of paper sheets prepared from CMC-metal oxides treated wood pulp.

that, the addition of CMC-Fe(III) complexes improves to slight extent the semiconductor property of wood pulp paper sheets, but the reverse trend is noticed for the case of HEC-Fe(III) and CMC-Zn(II) complexes. These observations are probably related to the magnetic moment, molar conductivity and electrical conductivity of metal and metal complexes [14, 22, 23].

TABLE II Activation energies, frequency factors, specific rate constants, residues and order of degradation of the main degradation stages of untreated and treated paper sheets

Type of additive	*Temp. range (°C)*	*DTG peak maxima (°C)*	E_a *(kJ/mol.)*	*A(sec.* $^{-1}$*)*	$K \times 10^{-6}$ *(min.* $^{-1}$*)*	*Residue, %*	"*n*"
–	239–377	332.6	98.552	2.66×10^5	22.53	19.229	0.5
HEC-$FeCl_3$ complex	193–358	305.0	60.922	4.81×10^2	69.40	43.138	0.0
CMC-$FeCl_3$ complex	203–354	320.6	75.860	7.92×10^3	36.26	42.820	0.0
CMC-Fe $(NO_3)_3$ complex	206–331	319.7	81.761	$2 .68 \times 10^4$	31.82	28.047	0.0
CMC-$LnCl_2$ complex	221–380	327.2	87.886	5.52×10^4	27.11	27.800	0.0
CMC-Fe_2O_3	245–354	336.4	120.133	1.51×10^7	11.20	24.900	0.5
CMC-ZnO	213–350	334.6	90.983	1.07×10^5	16.30	27.600	0.0

TABLE III Magnetic susceptibility and electrical conductivity of paper samples

Type of additive	*Mass suceptibility* ($c.g.s.$) $\times 10^{-6}$	*Electrical conductivity* ($Ohm^{-1}cm^{-1}$) $\times 10^{-10}$
–	–	2.85
HEC-$FeCl_3$ complex	0.483	7.03
CMC-$FeCl_3$ complex	9.386	2.31
CMC-$Fe(NO_3)_3$ complex	7.939	1.38
CMC-$ZnCl_2$ complex	0.269	4.01
CMC-Fe_2O_3	5.578	4.166
CMC-ZnO	2.871	5.61

By comparing the values of x_g of paper sheets prepared by adding CMC-Fe(III) complexes possess a relatively high magnetic property than that including iron oxide with CMC; while the paper sheet prepared by adding CMC-Zn(II) complex and CMC-ZnO have nearly the same magnetic property.

It is clear also that, the addition of CMC-Fe(III) and CMC-Zn(II) complexes improves the semiconductor property of paper sheet than paper sheet treated with CMC-metal oxides. Adding the complexes of CMC with $Fe(NO_3)_3$ and $FeCl_3$ achieved maximum improvement in the magnetic and semiconductor properties of paper sheets, respectively.

Strength and Water Resistance Properties

Table IV shows the percentages of changes in strength (breaking length, burst and tear factors) and water absorption properties (based on untreated paper sheets), in addition to the air permeability (ml/min) of all examined paper samples. The percentages of the change in the strength and water absorption properties of paper sheets prepared from chemically treated of soft-wood pulp or adding hydrophilic and hydrophobic additives [24, 25], are taken in consideration (Tab. V).

From Table IV it is clear that, the percentages of improving mechanical properties of paper sheets in the case of CMC-complex addition are higher than the case of HEC-complex. This is related to the nature of functional groups in cellulose ether (ligand), and consequently the bond strength of ferric ions with it [15].

For the variation of the percentage of change in strength properties of CMC complex-wood pulp paper sheets with changing the anion

TABLE IV Change percentages of strength properties, water absorption and air permeability of paper samples

	Change percentage				
Type of additive	*Breaking, length, m*	*Burst factor*	*Tear factor*	*Water absorption, %*	*Air permeability ml/min*
–	0.000	0.000	0.000	0.000	180
HEC-$FeCl_3$ complex	2.354	6.350	20.144	−10.856	230
CMC-$FeCl_3$ complex	34.874	64.500	42.019	−28.013	450
CMC-$Fe(NO_3)_3$ complex	46.68	75.325	47.960	−28.703	800
CMC-$ZnCl_2$ complex	55.294	82.703	25.955	−34.561	85
CMC-Fe_2O_3	28.187	83.950	47.358	–	320
CMC-ZnO	−9.9435	0.148	5.506	–	0.00

TABLE V Change percentages of strength properties and water absorption of previously treated paper samples [24, 25]

	Change percentage			
Paper samples	*Breaking length, m*	*Burst factor*	*Tear factor*	*Water* absorption, %*
Untreated wood pulp (WP)	0.000	0.000	0.000	0.000
Carboxymethylated W.P (D.S. 0.046)	−13.13	−74.07	55.54	−3.047
Wood pulp + CMC (D.S. 0.046)	14.77	−7.711	12.70	10.33
Acetylated wood pulp (Acetyl content 18.38%)	−55.31	−76.119	−75.06	−8.05
Wood pulp + 9% homopolymer (PAN)	−23.30	−6.99	–	4.83
PAN-grafted pulp (25 g AN/100WP)	−84.68	−85.83	−97.22	8.391
Wood pulp + 9% homopolymer(PMA)	−13.93	−38.47	–	9.964
PMA-grafted pulp (25 g MA/100 WP)	−46.30	26.16	−20.65	4.251

* Immersing time for determination of water absorption % is 2 hrs., at 23°C.
PAN = polyacrylonitrile,
PMA = polymethyl acrylate.

(Cl^{-1} and NO_3^{-1}) of ferric salts used for complex formation, Table IV shows that the percentages of improvement in the case of CMC-$Fe(NO_3)_3$ is higher than CMC-$FeCl_3$ complex addition. This result is probably related to the values of nephlauxetic parameter (β) of the used complexes. Whreas, the values of (β) in the case of CMC-$FeCl_3$ and CMC-$Fe(NO_3)_3$ complexes are 0.43 and 0.45, respectively [14], *i.e.*, a reduction in neuclar charge on the cation in the former complex is higher than latter ones [26]. Therefore, the Fe(III) ions of CMC-$FeCl_3$ complex is less probable to bridge the cellulose fiber surface compared with CMC-$Fe(NO_3)_3$.

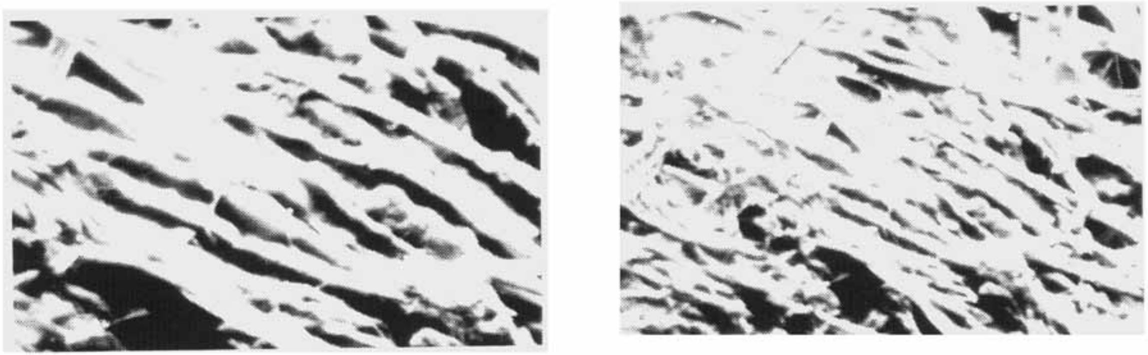
While, for the variation of the cation (Fe^{+3} and Zn^{+2}) of metal salt which was chelated with CMC, Table IV shows that, the percentages of improving in strength properties of paper sheet in the case of beater adding CMC-$ZnCl_2$ complex are higher than the case of adding CMC-$FeCl_3$ complex. This observation is related to change the type of combination between CMC with $ZnCl_2$ (ionic bond) and CMC with $FeCl_3$ (covalent coordinated bond), which also affected on the bridging of cellulose fibers through the metal of CMC-complexes [14, 15]. This view was emphasized from the values of decomposition temperatures and the activation energies of thermal degradation of paper sheets in Table II.

Table IV also shows that, paper sheets containing metal complexes have relatively high strength properties and high porous structure (from the SEM; Figs. 8, 9, and air permeability values) than those obtained from beater adding CMC-metal oxides.

By comparing the percentages of the change in strength and water absorption properties of the paper samples under investigation with those obtained from previously investigated paper samples [24, 25], Tables IV and V show that chemical treatment of soft wood pulp, either by chemical modification or adding some polymer additives, both have a great effect on the strength and water resistance properties. For the treatments which improve the strength properties of paper, *e.g.*, addition of CMC, the deterioration in the water resistance property is greater than that obtained from treating the pulp or adding some homopolymer additives, which lead to deteriorate the strength properties of the obtained paper sheets. However, in the case of using cellulose ether-metal complexes as beater additive, especially for the case of using CMC-Fe(III) complexes, the produced sheets possess both advantage properties (*i.e.*, improved the strength and water resistance properties).

The high strength and water resistance in addition to porous structure of CMC complex-wood pulp sheets prospect us that this new type of paper sheets can be used for the production of Nursery-plant boats.

Wood Pulp



HEC-FeCl, complex treated pulp

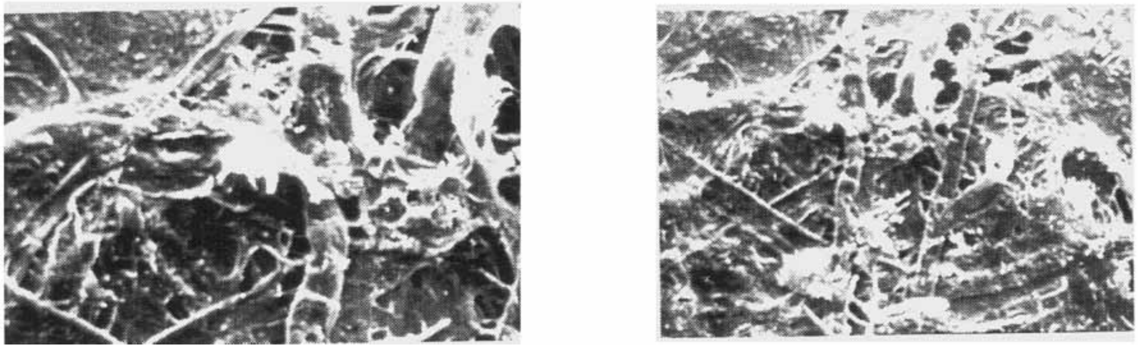
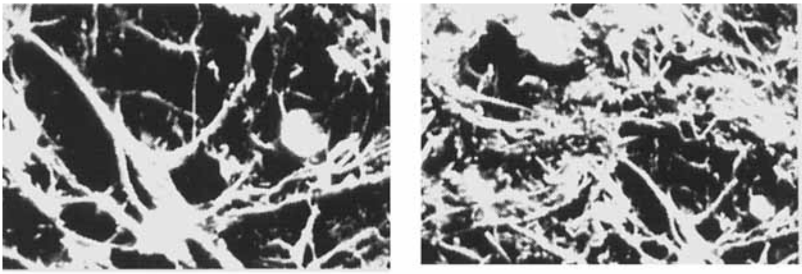
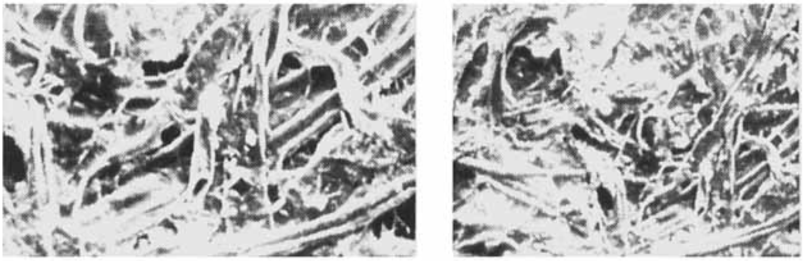


FIGURE 8 SEM photographs of paper sheets prepared from untreated and HEC-Fe(III) complex treated wood pulp.

CMC-FeCl$_3$ complex treated pulp



CMC-Fe(NO$_3$)$_3$ complex treated pulp



CMC-ZnCl$_2$ complex treated pulp

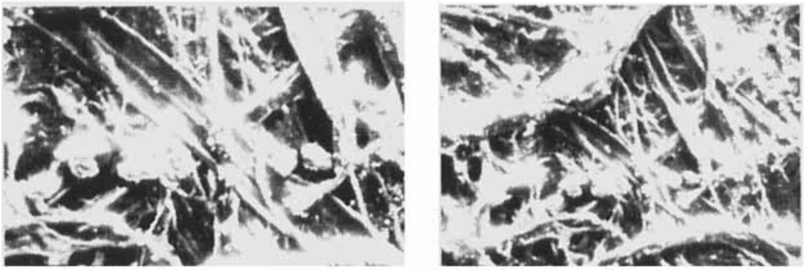


FIGURE 9 SEM photographs of paper sheets prepared from CMC-metal complexes treated wood pulp.

Biological Evaluation

From Table VI it is clear that, introducing Fe(III)- or Zn(II)-complexes to cellulose pulp improves the antimicrobial action of the

TABLE VI Anti-microbial action of paper samples on some microorganisms*

Paper sample with the used additives	*Salmonella typhi*	*Penicillum chrysogen*	*Candida albicous*	*Staphylococcus aureus*	*Escherichia coil*	*Pseudomoas aeruginosa*	*Aspergillu-sniger*	*Bacillus stabtilis*	*Saccoromyces cervisiae*
Wood pulp	–	–	–	–	–	–	–	–	–
HEC-$FeCl_3$ complex	–	–	–	0.45	–	–	–	0.45	–
CMC-$FeCl_3$ complex	–	0.6	–	0.55	–	–	–	0.45	–
CMC-$Fe(NO_3)_3$ complex	–	–	–	0.45	–	–	–	–	0.55
CMC-$ZnCl_2$ complex	–	–	–	1.05	–	–	0.55	–	0.45

*Diameter of unloaded diskette = 0.4 cm.

produced paper sheets. The most active paper sheet was that prepared from adding CMC-Zn(II) complex to wood pulp.

From all the foregoing results it could be concluded that, the application of cellulose ether-metal complexes as a new beater additives is successful for producing special paper sheets have flame retardancy, high strength, magnetic, semiconducting and water resistance properties, in addition to porous paper structure and antimicrobial action.

References

[1] Serebrenikov, P. P. (1934). *Chemical Methods of Fire*, Zbornik Trud, CNILCHI, **2**, 43.
[2] Schuyten, H. A. *et al.* (1955). *Ind. Eng. Chem.*, **47**, 1433.
[3] Shafizadeh, F., Lai, Y. Z. and McIntyre, C. R. (1978). *J. Appl. Polym. Sci.*, **22**, 1183.
[4] Gordon, L. N. (1990). "Fire and Polymers, Hazards Identification and Prevention", *Am. Chem. Soc.*, Washington, DC, p. 335.
[5] Singh, R., Arora, S. and Lal, K. (1996). *Thermochim. Acta*, **289**, 9.
[6] Marchessault, R. H., Rioux, P. and Louise, R. (1992). *Polymer*, **33**, 4024.
[7] Ziolo, R. F. (1985). US Patent 4474866 (1984). *Chem. Abstr.*, **2**, 15114.
[8] Sobon, C. A., Bowen, H. K., Broad, A. and Cavert, P. D. (1987). *J. Mater. Sci. Lett.*, **8**, 901.
[9] Calvert, P. D. and Mann, S. J. (1988). *J. Mater. Sci.*, **11**, 3801.
[10] Markblatt IV/29 Zellcheming (German Association of Cellulose Chemist and Engineering).
[11] Jayme, G. and Sarten, P. (1940). *Naturewise*, **28**, 822; *Z. Biochem.*, **308**, 109.
[12] The Institute of Paper Chemistry, Appleton. Wisconsin. Institute Method No. 428, Jan., 1951.
[13] Hosny, W. M., Basta, A. H. and El-Saied, H. (1997). *Polym. International*, **42**, 157.
[14] Rioux, P., Ricard, S. and Marchessault, R. (1992). *Pulp and Paper Sci.*, **18**, 39.
[15] El-Saied, H., Basta, A. H. and Abdel-Nour, K. N. (1997). *IJPM*, **36**, 131.
[16] The Institute of Paper Chemistry, Appleton and Wisconsin, Institute Method No. 411 (1952).
[17] Casey, J. P. (1981). "*Pulp and Paper Chemistry and Technology*", Vol. III, 3rd edn., A Wiley-Interscience Publication, New York, p. 1754.
[18] Abou-Zeid, A. A. and Shehata, Y. (1969). *Indian J. Pharmacy*, **31**, 72.
[19] Coats, A. W. and Redfern, J. R. (1964). *Nature*, **201**, 68.
[20] Basta, A. H., Sefain, M. Z. and El-Wakil, N. A. (1994). *Polym. Plast. Technol. Eng.*, **33**, 135.
[21] Hojo, H. S. and Arakawa, N. (1966). In: *Paper Presented at 15th High Polymer Conference (Japan). Nagoya*, Abstracts, p. 130.
[22] Abd-El-Messieh, S. L., Basta, A. H. and El-Saied, H., Submitted for Publication in *J. Mater. Sci.* (June, 1998).
[23] Lee, J. D. (1991). A Text Book of "*Concise Inorganic Chemistry*", 5th edition, London.
[24] Fahmy, Y. and El-Saied, H. (1974). *Holzforschung*, **28**, 29.
[25] Fahmy, Y. and El-Saied, H. (1974). *Holzforschung*, **28**, 61.
[26] Jorgensen, C. K. (1962). *Prog. Inorg. Chem.*, **4**, 73.