

## **THERMAL DECOMPOSITION OF NITROCELLULOSES DERIVED FROM WOOD AND COTTON: A NON-ISOTHERMAL THERMOGRAVIMETRIC ANALYSIS**

JEAN-JACQUES JUTIER and ROBERT E. PRUD'HOMME

*Groupe de Recherche sur les Macromolécules, Département de Chimie, Université Laval, Québec, Québec, G1K 7P4 Canada*

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### **ABSTRACT**

The thermal decomposition of nitrocellulose (NC) fibers derived from wood (two samples) and cotton (four samples) was followed using a non-isothermal thermogravimetric (TG) technique. The nitrogen content of the fibers ranged from 12.6 to 13.5%. Activation energies were calculated using various methods of analysis of the TG data including the conventional procedures (i.e., Ozawa's equation, Fatemi et al.'s and Popescu and Segal's methods) and a curve fitting treatment originally proposed by Eisenreich and Pfeil. No variation in activation energies is observed between NC dried fibers and NC films cast from acetone, tetrahydrofuran (THF) and ethyl acetate, whatever the nitrogen content of the sample. However, the catalytic effect of Pb(II) and Cu(II) salicylates on the thermal degradation of NC is demonstrated. Finally, using the TG curves for NC fibers and films, a subtracting procedure is proposed to differentiate the vegetal origin and the nitrogen content of nitrocellulose.

### **INTRODUCTION**

Following the first synthesis of nitrated cellulose (NC) by Pelouze [1] in 1838, there has been a fair amount of study devoted to its thermal decomposition which is complex owing to the formation of a large number of degradation products [2–5].

Using isothermal thermogravimetry (TG), Manelis et al. [5] described the thermal decomposition of pure NC as an autocatalytic process consisting of subsequent monomolecular and catalytic reactions. In contrast, noting the changes in the infrared spectra of a thin NC film as a function of time, Phillips et al. [6] approximated the rate of decomposition of NC by a first order equation with two or three branches.

Using TG and quantitative differential thermal analysis (DTA), Eisenreich and Pfeil [7,8] studied the effect of Pb(II) and Cu(II) salicylates salts on the thermal decomposition of NC in solid propellants. They noticed that those salts have a catalytic effect provided by the structural interaction of the catalyst with the NC.

Eisenreich and Pfeil [9] also studied the thermal decomposition of highly nitrated NC by non-isothermal techniques, combining TG, DTA, and infrared and Raman spectroscopies. They computed various kinetic parameters by a curve fitting procedure. Their results indicate that the thermal decomposition of NC is made up of an autocatalytic reaction, followed by a second-order simple reaction which leads to a charcoal-like residue. These two steps are separated by a discontinuity which appears at about 50% conversion. The autocatalytic process can, in turn, be divided into two different steps having equal activation energies that are equivalent to the dissociation energy of the O-NO<sub>2</sub> bond of simple nitrate esters. In all these studies, activation energies and pre-exponential factors range from 119 to 234 kJ mol<sup>-1</sup> and from 10<sup>18</sup> to 10<sup>24</sup> s<sup>-1</sup>, respectively, [5,9–11].

More recently, Lemieux and Prud'homme [12] compared the thermal decomposition behavior of several NC derived from wood and cotton by differential scanning calorimetry (DSC) and bomb calorimetry. Heats of decomposition, explosion and combustion of highly nitrated NC, containing from 12.6 to 13.5% N were measured. These authors observed that the average heats of decomposition and explosion of dried NC fibers increase slightly, whereas the average heat of combustion decreases slightly, with nitrogen content. The combustive action of oxygen and the inhibitory effect of nitrogen towards NC degradation were discussed.

In this work, several NC derived from wood and cotton are investigated using a dynamic thermogravimetry (TG) method in air and nitrogen atmospheres. Pure NC fibers and NC samples cast from tetrahydrofuran (THF), acetone and ethyl acetate are analyzed. The nitrogen content of the NC samples range from 12.6 to 13.5%. Kinetic methods (i.e., Ozawa's equation [13], Fatemi et al.'s [14] and Popescu and Segal's [15] methods) are combined with a curve fitting technique to calculate kinetic parameters; the values obtained with each of these methods are compared. The effect of Cu(II) and Pb(II) salts are finally discussed in relation with the origin and the nitrogen content of the samples.

## EXPERIMENTAL SECTION

### *Nitrocellulose samples*

Six nitrocellulose samples have been used in the present study. Their main characteristics are given in Table 1. It should be noted that the acronym NCW-1343 stands for a nitrocellulose (NC) derived from wood (W) and containing 13.43% of nitrogen; the acronym NCC-1350 stands for a nitrocellulose (NC) derived from cotton (C) and containing 13.50% of nitrogen; the other acronyms have a similar meaning.

The average length of the NC fibers used was determined by light

TABLE 1

Nitrocellulose samples used

Sample	Country of origin	Cellulose Source	%N	Molecular weight (GPC) ( $\text{kg mol}^{-1}$ )		Remarks
				$\overline{M}_w$	$\overline{M}_n$	
NCW-1342	Canada	Wood	13.42	405	117	High grade (Grade B) Expro Chemical Products Inc.
NCW-1262	Canada	Wood	12.62	342	145	Pyro (Grade A, Type I) Wood pulp (Rayonier Q-LD) Expro Chemical Products Inc.
NCC-1350	U.S.A.	Cotton	13.50	323	103	High grade (Grade B) U.S. Army Ballistic Research Laboratories
NCC-1314	Canada	Cotton	13.14	360	163	Military Blend (Grade C, Type I) sheeted cotton linters (Buckeye Corp.) Expro Chemical Products Inc.
NCC-1274	Australia	Cotton	12.74	309	125	Mechanically nitrated papered cotton linters (Shoalhaven) Mulwala Explosives Factory
NCC-1260	U.S.A.	Cotton	12.60	370	100	Pyro (Grade A, Type I) U.S. Army Ballistic Research Laboratories

microscopy using a calibrated eyepiece. The NC fibers derived from cotton or wood have similar average lengths, ranging between 15 and 25  $\mu\text{m}$  for the shortest fibers to between 300 and 500  $\mu\text{m}$  for the longest ones. The average length and average diameter of the fibers are the same whatever their nitrogen content.

Recently, Mann and Patrick [16] followed the esterification of cellulose fibers by scanning electron microscopy (SEM). The surface of the cotton linters and wood pulp fibers showed a greater porosity and degradation of their structure after nitration than they did before. Furthermore, cotton linters were found to be less damaged than wood pulp fibers. The typical NC sample derived from cotton linter used in this study is a long tube which is made up of fibrils coiled into an helix (Fig. 1A). The surface of this tube shows smooth-edged pores suggesting partial solvation of the cellulose during nitration [17]. All NC fibers derived from wood have a flattened ribbon shape with pits or pores typically seen in wood pulp cell walls (Fig.

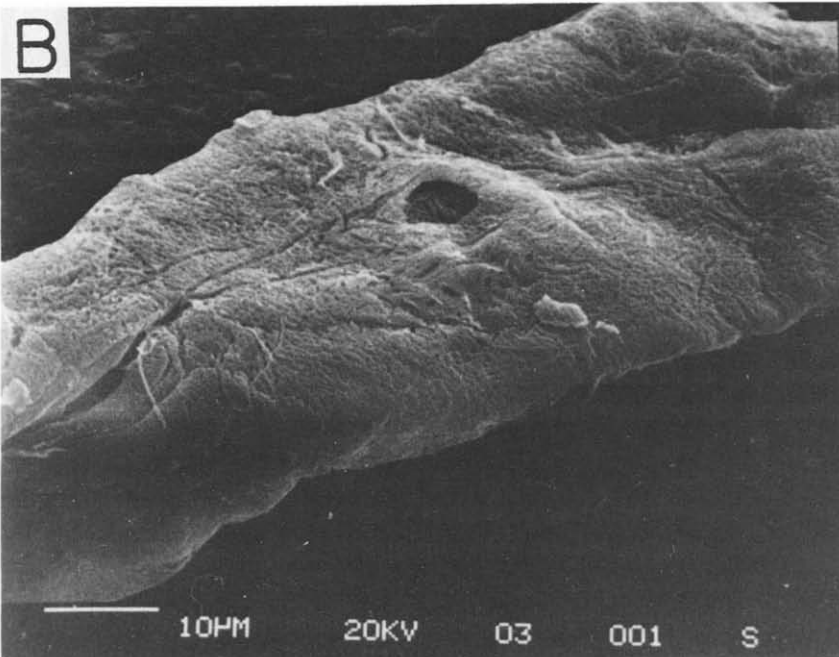
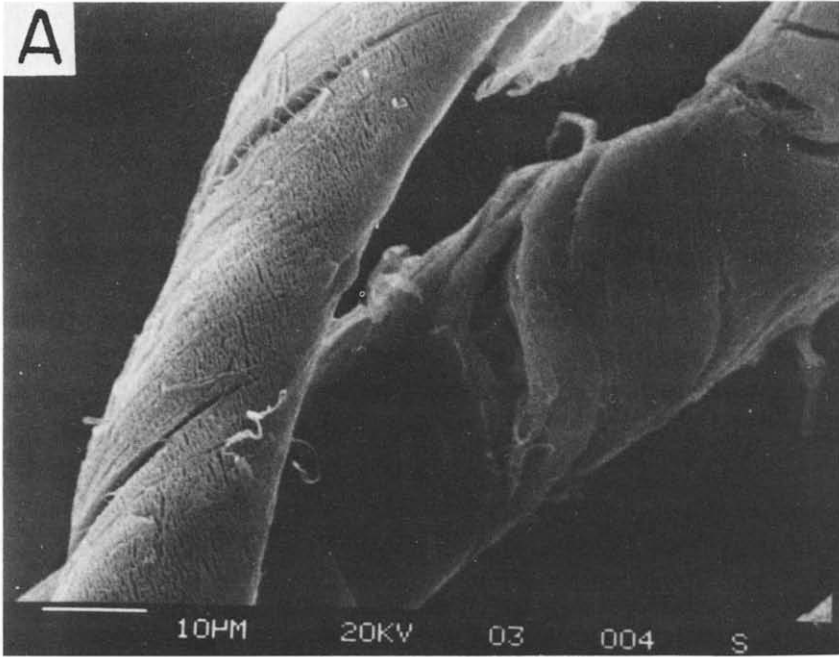


Fig. 1. Scanning electron micrographs of NC samples: A: nitrocellulose derived from cotton (NCC-1350); B: nitrocellulose derived from wood (NCW-1342).

1B). The surface of the NC fibers derived from wood also suggests partial solvation during nitration, with subsequent rapid drying [17].

### *Sample preparation*

The NC wet fibers were dried in a vacuum oven for several days, at room temperature as described in a recent paper [12]. NC solutions were prepared using freshly distilled THF, spectroscopic grade acetone or ethyl acetate, with dry fibers, and films were cast thereof. The resulting films were removed from petri dishes and dried in a vacuum oven until they reached a constant weight. NC samples were also prepared by casting films from NC solution in acetone to which about 4% (w/w) of Pb(II) salicylate or Cu(II) salicylate were added.

### *Thermogravimetric analysis*

The decomposition of NC was studied by dynamic thermogravimetry (TG) which was performed with a Perkin-Elmer TGS-2 instrument coupled to a System-4 Microprocessor Controller and a 3600 Thermal Analysis Data Station.

The experiments were conducted in air or nitrogen atmospheres, at a flow rate of  $40 \text{ ml min}^{-1}$ , with about 5 mg of sample. The temperature interval ranged from 400 to 660 K. The Pt/Pt-Rh thermocouple used to monitor the sample temperature was calibrated at the recommended alumel Curie temperature of 436 K for each set of operating conditions. Heating rates of 0.5, 1, 3, 5, 10 and  $20 \text{ K min}^{-1}$  were employed. The sample temperature and sample mass were continuously recorded and the first derivative of the mass-temperature curve was calculated. Under the conditions used [18], no self-heating or deflagration of the NC samples occurred. At the end of each experiment, the furnace tube and the balance were purged with oxygen. Results were considered to be satisfactory if, for a given sample, two consecutive TG curves could be superimposed under the same experimental conditions.

## THEORETICAL BACKGROUND

The data obtained in this study have been analyzed following the general rate equation

$$d\alpha/dt = kf(\alpha) \quad (1)$$

where  $\alpha$  is the degree of conversion,  $t$  the time, and  $k$  the rate constant. Equation (1) expresses the rate of conversion of the reaction  $d\alpha/dt$  at a constant temperature  $T$ .

Generally, for polymer degradation kinetics, the function  $f(\alpha)$  is given by

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

where  $n$  is the apparent order of reaction and the temperature dependence of the rate constant  $k$  is given by the Arrhenius expression

$$k = A \exp(-E/RT) \quad (3)$$

where  $E$  is the activation energy,  $R$  the gas constant and  $A$  a pre-exponential factor. Inserting eqns. (2) and (3) into eqn. (1), one gets

$$d\alpha/dt = A(1 - \alpha)^n \exp(-E/RT) \quad (4)$$

From eqn. (4), several methods of analysis have been proposed using TG curves at a single heating rate: for example, the Freeman-Carroll method [19] and the McCallum-Tanner method [20]. Other methods are based on the use of TG curves at several heating rates. Three methods of this sort were used in this article. The first one, due to Fatemi et al. [14], is identical with that of Kissinger [21]. For a linear heating rate  $\beta$  (i.e.,  $\beta = dT/dt$ ), eqn. (4) can be expressed as

$$d\alpha/dT = A/\beta(1 - \alpha)^n \exp(-E/RT) \quad (5)$$

Using the temperature  $T_m$  at the inflexion point of the weight loss curve, after rearrangements, one gets [14]

$$\ln(\beta/T_m^2) = -E/RT_m + \ln[AR/E(-df(\alpha)/d\alpha)_{\alpha_m}] \quad (6)$$

A plot of  $\ln(\beta/T_m^2)$  as a function of  $(1/T_m)$  then gives  $E$  from the slope of the straight line thus obtained.

The second method used is that of Ozawa [13] (or Flynn and Wall [22]) which is described by the equation

$$\log(F(\alpha)) = \log(AE/R) - \log(\beta) - 2.315 - 0.4567(E/RT) \quad (7)$$

$E$  can then be obtained from a plot of  $\log(\beta)$  as a function of  $T^{-1}$  for a given degree of conversion  $\alpha$ . In addition,  $A$  can be calculated from the intercept on the  $\log(\beta)$  axis.

The last method used is due to Popescu and Segal [15] and it is formally identical with that of Ozawa [13], except that it uses uniquely  $\alpha_m$  and  $T_m$  instead of a large number of  $\alpha$  and  $T$ . From several thermograms taken at different heating rates  $\beta_i$  for the same sample, two parallel lines to the two axes are drawn passing through the inflexion point of the curve ( $\alpha_{m_1}, T_{m_1}$ ). From these two parallel lines, a temperature  $T_i$  is found at each heating rate  $\beta_i$  by keeping  $\alpha$  constant ( $\alpha = \alpha_{m_1}$ , or  $\alpha_{m_2}$ , or  $\alpha_{m_3}$ , etc.); on the other hand a value of  $\alpha_i$  is found at each heating rate  $\beta_i$  by keeping  $T_i$  constant ( $T = T_{m_1}$ , or  $T_{m_2}$ , or  $T_{m_3}$ , etc.). After separation of the terms and integration of eqn. (4) the following equation is obtained

$$\log(\beta_2/\beta_1) = 0.4343(E/R)(1/T_{m_1} - 1/T_2) \quad (8)$$

Solving eqn. (7) will give the kinetic parameter  $E$ .

The data obtained in this study have also been analyzed using the autocatalytic equation proposed by Manelis et al. [5] and Eisenreich et al. [9] for the thermal degradation of NC. Under non-isothermal conditions, they derived the following differential equation [5,9].

$$\beta d\alpha/dT = -k_1(T)\alpha - k_2(T)\alpha(1 - \alpha) \quad (9)$$

whose solution is

$$\alpha(T) = \frac{\exp\{-[(A_1/\beta)S_1(T) + (A_2/\beta)S_2(T)]\}}{1 - (1/\beta)\int_{T_0}^T k_2(T)\exp\{-[(A_1/\beta)S_1(T) + (A_2/\beta)S_2(T)]\}dT} \quad (10)$$

Where  $S(T)$  is the integral of the Arrhenius function

$$S(T) = \int_{T_0}^T \exp(-E/RT)dT \quad (11)$$

and  $T_0$  the initial temperature.  $S(T)$  was calculated using the first five terms of a semi-convergent series [23], and  $k_2(T)$ , which is the rate constant of the first-order autocatalytic equation, is defined by

$$k_2(T) = A \exp(-E/RT) \quad (12)$$

The integral involved in eqn. (10) was computed numerically using Simpson's rule. The complete description and resolution of eqn. (10) is given in ref. 23.

Non-isothermal studies [9] show that the thermal degradation of NC proceeds in two main steps. Two rate laws are then required to describe this decomposition process which is made of a first-order autocatalytic reaction, followed by a simple order reaction. The first autocatalytic step is described by eqn. (10) whereas the rate equation for a  $n$ th order simple kinetics is

$$\beta d\alpha/dT = -k(T)\alpha^n \quad (13)$$

where  $k(T)$  is the rate constant of the decomposition process defined by eqn. (12). The solution of eqn. (13) is

$$\alpha(T) = [1 + (n - 1)\beta^{-1}AS(T)]^{1/(1-n)} \quad (14)$$

In this study, the kinetic parameters for the decomposition of NC were determined by fitting eqns. (10) and (14) to the experimental TG curves using a non-linear least-squares program [24].

## RESULTS

Figure 2 shows the thermal decomposition curves of several of the NC used in this study. Those thermograms were obtained using about 5 mg of dried NC fibers, at a heating rate of 1 K min<sup>-1</sup> in a nitrogen atmosphere.

No significant difference is observed between the thermal decomposition of NC fibers of 5 or 10 mg, contrary to the results reported by Paulik et al. [18] and Pfeil and Eisenreich [25]. However, we noticed that the specific gravity of the sample has an important effect on the shape of the TG curve. The degradation curves of high bulk density samples (highly pressed fibers) exhibit a sharp transition at the temperature of maximum reaction rate, while the degradation curves of low bulk density samples (fluffy mat of fibers) give the typical shape shown in Fig. 2.

The TG curves of all NC fiber samples investigated have a sigmoidal shape, with decomposition starting at about 400 K, the maximum reaction rate being close to 464 K and the end of the degradation occurring at about 530 K. Between 400 and 470 K, the curves are not significantly different in view of the experimental error involved with this sort of measurement.

The weight losses shown in Fig. 2 are slow until a conversion of nearly 10% at about 450 K. Between 450 and 470 K, the weight losses become rapid, but as soon as 50 or 60% of the initial weight is lost, a slower reaction takes place leading to a charcoal residue. For NCW-1262 and NCW-1342, the residue obtained corresponds to 18.7 and 14.5% of the initial weight, respectively, while for NCC fibers it is smaller: 8.8 and 12.9% for NCC-1350 and NCC-1260, respectively. For NCC-1314, the TG curve, between 470 and 530 K, is intermediate between those of NCC-1350 and NCC-1260 fiber samples because NCC-1314 is a blend prepared from two NCs having smaller and larger nitrogen contents. Finally, NCC-1274 fibers give a residue corresponding to 18.3% of the initial weight, a value which is in the same range as those found for NCW fibers. This difference in residual weight may be due to a different preparation method used for this sample [12].

Additional studies were carried out in air and the resulting TG curves are similar to the ones obtained under a nitrogen atmosphere. No significant difference is observed with the NC vegetal origin or nitrogen content, with the exception of the residual weight at 530 K: NCW fibers produce a residue 1.5 times smaller than that found in a nitrogen atmosphere while the NCC fibers (except NCC-1274) give similar residues in air and nitrogen atmospheres. In other words, NCC fiber samples in air and in nitrogen atmospheres, and NCW fiber samples in air, give similar residues at 530 K.

Representative thermograms corresponding to the thermal degradation of NCW-1262 fibers in a nitrogen atmosphere are given in Fig. 3 for heating rates of 0.5, 1, 3, 5, 10 and 20 K min<sup>-1</sup>. The other samples give similar thermograms at the same heating rates. The curves are shifted to higher temperatures with increasing heating rates, as is expected from the kinetic theory. In general, the weight loss at the temperature of the maximum reaction rate does not change and the residual weight ( $T = 530$  K) of the sample does not vary with the heating rate, except with NCC-1260 and NCC-1350 samples where it varies slightly.

The curves shown in Fig. 4 are the result of a subtraction between two TG



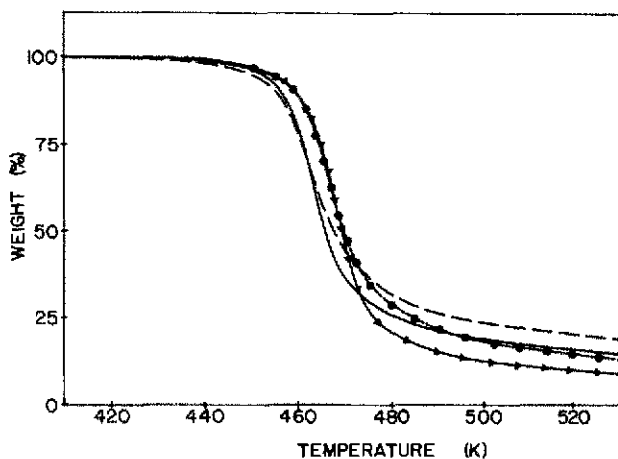


Fig. 2. TG curves for the decomposition of NC dried fibers ( $\approx 5$  mg) in a nitrogen atmosphere at a scan rate of  $1 \text{ K min}^{-1}$ : — NCW-1342; - - - NCW-1262; ●—● NCC-1260; ▲—▲ NCC-1350.

curves for NC fiber samples of two different vegetal origin and/or nitrogen content. By subtracting two NC thermograms having the same vegetal origin, a sigmoidal difference curve is obtained. In contrast, when the same procedure is carried out with two NC thermograms having different vegetal origins, the resulting curve has a U-shape, whatever might be the nitrogen content of these samples, except for the NCC-1274 fiber sample which always gives a U-shaped difference curve, whatever might be the vegetal origin of the second NC sample. We have seen before that the behavior of this particular NC sample is often different from that of the other NC

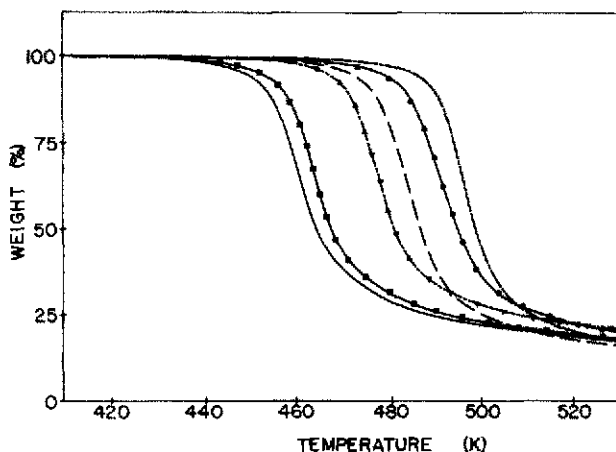


Fig. 3. Typical TG curves for NCW-1262 heated in nitrogen at various heating rates: —  $0.5 \text{ K min}^{-1}$ ; ■—■  $1 \text{ K min}^{-1}$ ; ▲—▲  $3 \text{ K min}^{-1}$ ; - - -  $5 \text{ K min}^{-1}$ ; ●—●  $10 \text{ K min}^{-1}$ ; - - -  $20 \text{ K min}^{-1}$ .

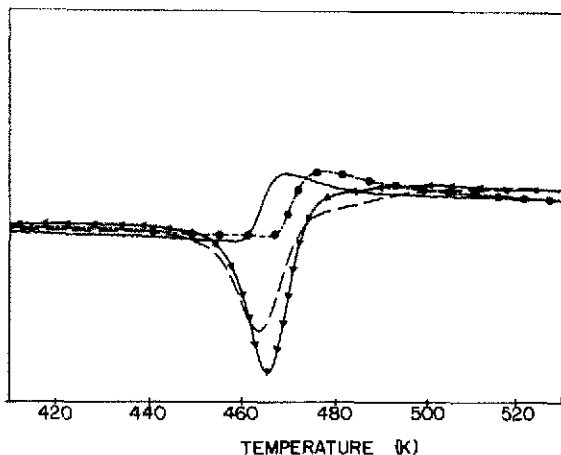


Fig. 4. Subtraction curves between various NC dried fibers heated in nitrogen at  $1 \text{ K min}^{-1}$ :  $\blacktriangle$ — $\blacktriangle$  (NCW-1342)–(NCC-1350); — (NCW-1262)–(NCC-1260); - - - (NCW-1262)–(NCW-1342);  $\bullet$ — $\bullet$  (NCC-1260)–(NCC-1350).

samples investigated. This behavior has been observed for each of the heating rates which were used in this study.

The thermal degradation of NC films cast from acetone, THF and ethyl acetate was also carried out in air at a heating rate of  $0.5 \text{ K min}^{-1}$ . The resulting thermograms have a sigmoidal shape identical to those obtained using dried fibers. However, the residue observed at 530 K is more important in most cases than the one obtained with dried fibers.

NC films of different origins cast in acetone and THF exhibit almost identical decomposition curves whatever their nitrogen content. However, NCC films cast from ethyl acetate exhibit decomposition curves which are shifted to higher temperatures by about 5 K as compared to the corresponding NCW decomposition curves, even if they can be superposed after shifting. Furthermore, the residual weight at 530 K varies with nitrogen content: NCC and NCW samples having a low nitrogen content (12.6% N) are characterized by a 16% residue while, for higher nitrogen contents (13.4% N), this residual weight decreases to 10% of the initial weight.

Whatever samples are compared, subtracting the TG curve of a NC film cast from acetone or THF from the TG curve of NC dried fibers gives either a U-shaped or a sigmoidal difference curve which are not related to the vegetal origin or the nitrogen content of these nitrocelluloses. However, if the TG curve of the NCW-1262 film cast from ethyl acetate is subtracted from the TG curve of NC dried fibers (Fig. 5A), it can be seen that the shape of the difference curve changes with the vegetal origin of the NC fiber sample. On the other hand, if the TG curve of a NCW-1342 film cast from ethyl acetate is subtracted from the TG curve of NC dried fibers (Fig. 5B), differences can be observed between the subtraction curves involving NC

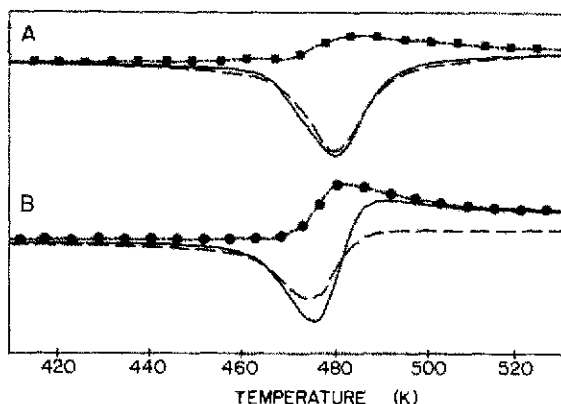


Fig. 5. Subtraction curves between a NC film cast from ethyl acetate and NC dried fibers heated in air at  $0.5 \text{ K min}^{-1}$ : A: — (NCW-1262)-(NCC-1260); - - - (NCW-1262)-(NCW-1342); ■—■ (NCW-1262)-(NCC-1350); B: — (NCW-1342)-(NCC-1260); - - - (NCW-1342)-(NCW-1262); ●—● (NCW-1342)-(NCC-1350).

samples derived from wood and having a high nitrogen content (13.4% N) and NC samples derived from cotton and having a low nitrogen content (12.6% N).

Finally, the effect of various salts on the thermal decomposition of NC was studied: the degradation of NC film cast from acetone with 4% (w/w) of either Pb(II) or Cu(II) salicylate was studied in air at a heating rate of  $0.5 \text{ K min}^{-1}$ . The resulting thermograms have an identical shape as the ones given in Fig. 2. The relative position of the various curves does not permit us

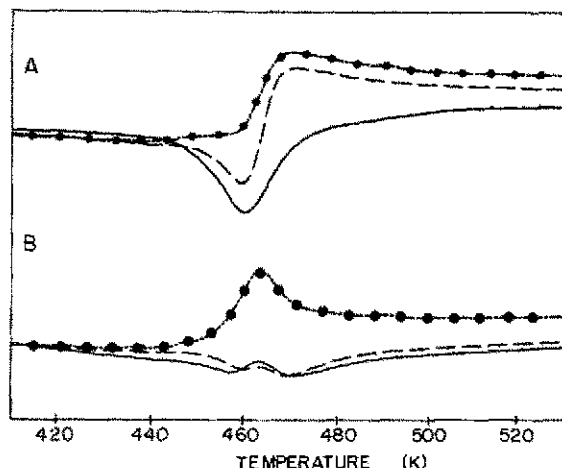


Fig. 6. Subtraction curves between various NC films cast from acetone with A: 4% (w/w) Pb(II) salicylate and B: 4% (w/w) Cu(II) salicylate. — (NCW-1262)-(NCC-1350); ●—● (NCW-1262)-(NCW-1342); - - - (NCW-1262)-(NCC-1260).

to distinguish one sample from the other. Furthermore, modifying the quantity of salt present in the sample does not change the shape of the TG curve and does not shift it significantly.

However, the widths at half-height of the derivative curves (DTG) obtained using various NC samples with salts added are larger than the ones measured using the same samples without any salt. Thus, activation energies corresponding to the thermal decomposition of NC samples with salts added are smaller than the ones found for the same samples without any salt. This shows the catalytic effect of Pb(II) or Cu(II) salicylate on the thermal degradation of all NC samples investigated.

Once again, the subtraction procedure proved to be efficient. If the TG curves of NCW and NCC films cast from acetone with Pb(II) salicylate added are each subtracted from the others (Fig. 6A), it can be seen that the shape of the difference curves change with the vegetal origin of the NC sample. A U-shaped difference curve is obtained when one compares the NC samples derived from wood with the NC samples derived from cotton. When two different NCW or two different NCC samples are compared one another this gives a sigmoidal curve. The results are quite similar by either using Pb(II) or Cu(II) salicylate (Fig. 6B).

## DISCUSSION

The thermogravimetric data obtained in this study have been analyzed using several of the kinetic methods described in the theoretical section. In keeping with the usual statistical practice, the data presented have been assigned error limits at a 95% confidence limit.

Table 2 gives the mean value of the activation energy for the decomposition of NC fibers calculated using Ozawa's, Popescu and Segal's and Fatemi et al.'s methods. The values obtained with these three methods are in fair

TABLE 2

Apparent activation energies for the thermal decomposition of NC derived from cotton and wood ( $\text{kJ mol}^{-1}$ )

Sample	Method		
	Fatemi et al. [14]	Popescu and Segal [15]	Ozawa [13]
NCW-1262	$179 \pm 8$	$182 \pm 7$	$190 \pm 6$
NCW-1342	$184 \pm 7$	$184 \pm 7$	$188 \pm 7$
NCC-1260	$192 \pm 8$	$197 \pm 8$	$181 \pm 9$
NCC-1350	$198 \pm 8$	$211 \pm 8$	$184 \pm 8$
NCC-1274	$185 \pm 7$	$188 \pm 7$	$168 \pm 5$
NCC-1314	$195 \pm 8$	$203 \pm 8$	$190 \pm 8$

agreement, and not very different from one sample to the other. They are also in agreement with the literature data which range from 119 to 234 kJ mol<sup>-1</sup> [5,6,9–11]. Studies by Phillips et al. [6] on NCs with a nitrogen content ranging from 11.01 to 13.96% showed no variation of the activation energy with the nitrogen percentage, the average value being 187.5 kJ mol<sup>-1</sup>. Activation energies reported by Manelis et al. [5] and Eisenreich and Pfeil [9] were all equal to 180 kJ mol<sup>-1</sup>, even if the nitrogen content of these samples differed. However, it is seen from Table 2 that NCs derived from cotton have a slightly greater activation energy than the ones obtained for NCs derived from wood (except again with NCC-1274).

While Ozawa's equation is applicable to all points on the TG curves, Popescu and Segal's and Fatemi et al.'s methods use only one point, i.e., the point of maximum reaction rate, and are therefore regarded, in some respects, as having limited applicability. However, Table 2 reveals that these equations, despite this apparent inadequacy, are giving activation energies that are in close agreement with those obtained with Ozawa's method for NC samples.

Other methods of calculation, like the Freeman–Carroll equation [19] or the MacCallum–Tanner equation [20], have also been used to analyze the data obtained, but the activation energies thus obtained were much higher than the literature data. This indicates that the selection and use of an analytical method to solve a complex thermal degradation process is not an easy task and that all methods available are not equivalent. However, the reasons for this discrepancy observed using some of the popular methods for NC data is not clear at the present time.

The activation energy and the pre-exponential coefficient of a kinetic reaction can also be determined by fitting a theoretical curve with the experimental data as done by Eisenreich and Pfeil [9]. Their results suggest that the thermal decomposition of a NC having a nitrogen content of 13.3% can be divided into two parts: the first part is described by a first-order autocatalytic reaction while the second part is defined as a second-order simple reaction. Both processes are separated by a discontinuity unto the decomposition curve, occurring at a 50% conversion.

Tables 3 and 4 list calculated results obtained by fitting eqn. (10) to the experimental data of NC fibers and NC films cast from acetone, THF and ethyl acetate. We have verified that eqn. (10) predicts the degradation process of the NCs investigated up to a temperature corresponding to the maximum rate reaction. Beyond this temperature, eqn. (14) satisfactorily describes the end of the thermal decomposition. In fact, by using either a second-order reaction or a third-order reaction, we obtained similar results because both theoretical curves have a similar slope when the conversion lies between 50 and 0%. Therefore, the results reported herein for the first part of the TG curve are of the same order of magnitude as the data reported by Eisenreich and Pfeil [9], for all samples studied.

TABLE 3

Kinetic parameters of the first-order autocatalytic reaction of NC fibers <sup>a</sup>

Sample	Weight (mg)	$E_1$ (kJ mol <sup>-1</sup> )	log $Z_1$	$E_2$ (kJ mol <sup>-1</sup> )	log $Z_2$	Notes
NCW-1262	5	175.8	16.1	180.1	17.5	This work
NCW-1342	5	175.9	16.1	179.5	17.5	This work
NCC-1260	5	179.6	16.6	177.8	17.5	This work
NCC-1350	5	178.3	16.5	179.4	17.5	This work
NCC-1274	5	177.3	16.3	178.6	17.7	This work
NCC-1314	5	178.3	16.7	176.5	17.4	This work
NC-13,3	5	174.6	16.3	176.7	17.5	Ref. 23
NC-13,3	5	178.3	16.6	175.4	17.5	Ref. 8
NC-12,6	5	196.8	19.0	129.8	12.0	Ref. 5 (isothermal)

<sup>a</sup> Heating rate: 0.5 K min<sup>-1</sup> in air for NC dried fibers.

In general, activation energies (Table 3) obtained by curve fitting procedure are slightly smaller than the ones calculated using conventional methods (Table 2). The dissociation energy of the O-NO<sub>2</sub> bond of simple nitrate esters ranges from 151 to 167 kJ mol<sup>-1</sup> [2-4,6,26,27] but the higher value found in this study (178 kJ mol<sup>-1</sup>) corresponds to what is expected for a solid ester [4].

TABLE 4

Kinetic parameters of the first-order autocatalytic reaction of NC films cast from a solvent

Sample	$E_1$ (kJ mol <sup>-1</sup> )	log $Z_1$	$E_2$ (kJ mol <sup>-1</sup> )	log $Z_2$	Solvent used for casting
NCW-1262	181.5	16.6	181.7	17.6	acetone
NCW-1342	181.3	16.6	182.1	17.6	
NCC-1260	180.8	16.9	182.6	17.6	
NCC-1350	180.3	16.7	184.8	17.7	
NCC-1274	181.3	16.6	182.0	17.4	
NCC-1314	180.5	16.7	183.2	17.5	
NCW-1262	181.8	16.8	182.5	17.8	THF
NCW-1342	181.9	16.8	181.2	17.5	
NCC-1260	184.9	16.8	182.0	17.8	
NCC-1350	182.3	16.7	181.9	17.6	
NCC-1274	181.6	16.8	182.3	17.7	
NCC-1314	182.1	16.7	181.8	17.6	
NCW-1262	181.3	16.9	181.8	17.6	ethyl acetate
NCW-1342	181.6	16.9	180.9	17.5	
NCC-1260	182.5	16.8	182.4	17.6	
NCC-1350	182.6	16.8	180.8	17.3	
NCC-1274	181.5	16.8	181.7	17.5	
NCC-1314	182.5	16.6	181.1	17.4	

TABLE 5

Kinetic parameters of the first-order autocatalytic reaction of NC films cast from acetone

Sample	$E_1$ (kJ mol <sup>-1</sup> )	log $Z_1$	$E_2$ (kJ mol <sup>-1</sup> )	log $Z_2$	Additive added to the film (4% (w/w))
NCW-1262	155.7	14.0	159.5	15.3	Pb(II) salicylate
NCW-1342	149.1	13.3	165.0	16.0	
NCC-1260	155.1	13.8	160.9	15.4	
NCC-1350	156.0	13.9	163.3	15.6	
NCC-1274	154.3	13.7	160.1	15.5	
NCC-1314	155.2	13.8	162.4	15.6	
NCW-1262	181.5	16.6	181.7	17.6	without salt
NCW-1342	181.3	16.6	182.1	17.6	
NCC-1260	180.8	16.9	182.6	17.6	
NCC-1350	180.3	16.7	184.8	16.7	
NCC-1274	181.3	16.6	182.0	17.4	
NCC-1314	180.5	16.7	183.2	17.5	
NCW-1262	158.3	14.3	157.4	15.1	Cu(II) salicylate
NCW-1342	152.7	13.7	154.6	14.9	
NCC-1260	156.2	13.8	160.9	15.6	
NCC-1350	153.6	13.4	161.6	15.7	
NCC-1274	158.4	14.1	156.7	15.0	
NCC-1314	154.2	13.8	160.7	15.5	

NC films cast from THF, acetone or ethyl acetate show slightly larger activation energies as compared to the ones obtained for NC dried fibers, indicating that it is possible to change slightly the decomposition behavior of NCs by exposing them to solvents which are likely to be retained to various degrees by the NC molecules.

The addition of Pb(II) or Cu(II) salicylates to NC has a catalytic effect towards NC thermal degradation. The results listed in Table 5 show that there is a decrease of the activation energy of about 25 kJ mol<sup>-1</sup> going from NC films cast without salts to NC films cast with salts. In addition, the degradation rate constant of NC films cast with salts is three times larger than that measured for NC films cast without salts, these values being independent upon the amount of salt added.

By subtracting two thermograms of NC one from the other, it has been demonstrated that it is possible to identify the vegetal origin and, in certain cases, the nitrogen content of a nitrocellulose (except with NCC-1274). For example, when NCW fibers are compared with NCC fibers (Fig. 4), one obtains a U-shaped difference curve while two thermograms of NC fibers having the same vegetal origin gives a sigmoidal curve. On the other hand, if thermograms of NC films cast from ethyl acetate are subtracted from those of NC fibers (Fig. 5), one observes a difference curve in which the shape changes with the nitrogen content and the vegetal origin of nitrocelluloses.

In particular, when the subtracting procedure is carried out with two NCs having different vegetal origins but the same nitrogen content, the resulting curve has a U-shape. Thus, comparing, on the one hand, the NC fiber thermograms and comparing them, on the other hand, with those of NC films cast from ethyl acetate provides, in all cases, the vegetal origin of an unknown NC and provides, in some instances, its nitrogen content (except again with NCC-1274).

Finally, we have observed that the physical aspect of the residue obtained after thermal degradation is different for NCs derived from wood and those derived from cotton, whatever their nitrogen content: the NCs derived from wood decompose into a powdery charcoal while that derived from cotton, including the NCC-1274 sample, give a rather tarry residue. Additional work is being pursued in order to elucidate the relationship between residue composition and nitrocellulose origin.

## CONCLUSIONS

Non-isothermal TG analysis can be used to study the thermal decomposition of nitrocellulose. In this article, measurements were carried out for six different samples, two derived from wood (NCW) and four derived from cotton (NCC), all having a nitrogen content varying between 12.6 and 13.5%.

Activation energies of this reaction were calculated using various methods. The methods suggested by Fatemi et al., Popescu and Segal, and Ozawa, all requiring thermograms at several heating rates, proved to be satisfactory and gave values, for dried fibers, ranging from 179 to 198, from 182 to 211 and from 168 to 190 kJ mol<sup>-1</sup>, respectively. A curve fitting method indicated that the thermal decomposition of NC can be divided in two parts: the first one is described by an autocatalytic kinetic reaction, which is followed by a simple-order reaction. Activation energies for the autocatalytic are close to 177 kJ mol<sup>-1</sup> for all samples.

The catalytic effect of Pb(II) or Cu(II) salicylates was also demonstrated. A decrease of 15% in the activation energy is observed between NC films cast without salts and NC films cast with salts and the rate constant for this reaction is three times larger when Pb(II) or Cu(II) salicylates are added to the films.

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