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COMPLEXES OF NITROCELLULOSE WITH CUPRIC CHLORIDE

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COMPLEXES OF NITROCELLULOSE WITH CUPRIC CHLORIDE

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the square root of  $X^*$

ABSTRACT

The cupric chloride (CC) effect on the viscosity of nitrocellulose (NC) in an acetone solution was studied for various military and commercial type NC samples obtained from different suppliers. The NC samples were produced from wood and cotton cellulose with a nitrogen content between 11.0 and 13.5% and a molecular weight ranging from 20,000 to 800,000. The study was carried out using different NC and CC concentrations and at different shear rates. The addition of CC to the NC solution causes an increase of the viscosity as a function of time due to the complex formation between NC and CC which is accomplished in two stages, each with a specific rate constant. The variation of the viscosity with the shear rate followed a pseudoplastic non-Newtonian behaviour. An empirical factor, the "Cupric Chloride Parameter" (CCP), is computed from the intrinsic viscosity of the polymer as well as from the kinetic parameters of the complex formation and the weight fraction of CC relative to NC,  $X^*$ , determined at the saturation point. The CCP is characteristic of the NC sample and can be related to the cellulose source (wood or cotton) and nitrogen content. The value of  $X^*$  can be used as a parameter to elucidate structural differences among NC samples.

RÉSUMÉ

L'effet du chlorure cuivrique (CC) sur la viscosité de la nitrocellulose (NC) en solution dans l'acétone a été étudié pour plusieurs échantillons de NC, de types militaire et commercial, obtenus de différents fournisseurs. Les échantillons de NC ont été produits à partir de la cellulose du bois et du coton, avec un pourcentage d'azote entre 11.0 et 13.5% et un poids moléculaire compris entre 20,000 et 800,000. L'étude a été effectuée en utilisant différentes concentrations de NC et de CC et à différents gradients de vitesse. L'addition de CC à une solution de NC produit une augmentation de la viscosité en fonction du temps attribuable à la formation d'un complexe entre la NC et le CC qui s'accomplit en deux étapes ayant chacune une constante de vitesse spécifique. La variation de la viscosité avec le gradient de vitesse était conforme à un comportement pseudo-plastique non-Newtonien. Un facteur empirique, le "Paramètre chlorure cuivrique" (PCC), est calculé à partir de la viscosité intrinsèque du polymère ainsi que des paramètres cinétiques pour la formation d'un complexe et de la fraction pondérale de CC par rapport à la NC,  $X^*$ , déterminés au point de saturation. Le PCC est caractéristique de l'échantillon de NC et peut être relié à l'origine de la cellulose (bois ou coton) et au pourcentage d'azote. La valeur de  $X^*$  peut servir de paramètre pour élucider des différences de structure entre les échantillons de NC.

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NOMENCLATURE

a	the exponent in the Mark-Houwink relation
A	calibration constant for the Rotational Viscometer
C	the NC concentration expressed in wt-%
CC	cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ )
CCP	cupric chloride parameter
G	shear rate
GPC	gel permeation chromatography
HG	high grade
IR	infrared
$k_i, k_f$	the initial and final slopes respectively for the graph of $\log (\eta/\eta_0)$ vs t
$k_i^*, k_f^*$	the values of $k_i$ and $k_f$ respectively at the saturation point
K	Mark-Houwink parameter
LALLS	low-angle laser light scattering
m	the CC concentration expressed in wt-%
$M_w$	the weight average molecular weight
M	the molecular weight
NC	nitrocellulose
P	shear stress
S	scale reading for the Rotational Viscometer
t, $t_{gel}$	the time and gelling time respectively
U	speed factor for the Rotational Viscometer
X	the CC weight fraction relative to NC
$X^*$	the critical value of X obtained at the saturation point
$\eta, \eta_0$	the viscosity at time t and at t = 0 respectively

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NOMENCLATURE (Contd)

$\eta_G, \eta_{G_0}$  the viscosity at G shear rate and at zero shear rate  
respectively

$[\eta]$  the intrinsic viscosity

## 1.0 INTRODUCTION

It is well known that a variety of metallic and inorganic salts (Ref. 1) and oxides (Ref. 2) as well as free metals (especially Cu) can modify considerably the properties of nitrocellulose (NC) in solution. The addition of inorganic salts to NC solutions causes a viscosity increase which is followed by gelation and, eventually (in many cases), by syneresis (Ref. 3).

Campbell and Johnson (Ref. 4) found that the rate of gelling increased with the nitrogen content of NC indicating that residual hydroxyl groups were not directly involved in the gelation process. The gel formation seems to be due to the formation of a complex between the metallic salt and NC where cross-links are formed between the nitrate groups of adjacent NC chains. The rate of the association process followed an approximately first-order law and was accelerated by an increase in temperature.

Vodyakov (Ref. 5) found that the cross-linker concentration is approximately proportional to the nitrogen content of NC. Bullock et al (Ref. 6) observed that the increase in the viscosity of the NC solution with the addition of lead  $\beta$ -resorcylate is proportional to the molecular weight of NC. Jullander et al (Ref. 1) studied the cross-linking of NC solutions by means of titanium tetrachloride and found that cross-links are formed between unesterified hydroxyl groups of adjacent NC chains.

The object of this work is to relate the kinetics of complex formation between NC and cupric chloride (CC) to the structure, molecular weight and nitrogen content of NC as well as to the cellulose source (wood or cotton). For this purpose, the CC effect on the viscosity of NC in an acetone solution was studied for various wood and cotton NC samples of military and industrial grades, with different  $\bar{X}_N$  and molecular weights and obtained from different suppliers. The study

was carried out at different shear rates and using different NC and CC concentrations. This study yielded some important empirical parameters which enable us to differentiate between NC samples mainly according to their structure and cellulose origin.

This work was performed at DREV between March 1982 and March 1984 under PCN 21C07, Gun Propellants.

## 2.0 EXPERIMENTAL

### 2.1 Samples

The characterized NC samples are listed in Table I. The first eleven samples are typical of military applications whereas the last six samples are typical of commercial use. The reported values for the nitrogen content of the NC samples were provided by the suppliers.

The first three samples were obtained from Australia. Sample 1 was produced by the Explosives Factory at Maribyrnong from Maryvale pine pulp wood paper. Sample 2 was an experimental lot produced at Mulwala Explosives Factory from Australia Shoalhaven papered cotton linters. Sample 3 was a pyro wood NC made from Rayonier Q alpha cellulose board.

Samples 4, 5, 6 and 7 were obtained from EXPRO Chemical Products in Valleyfield, Québec, Canada. Samples 4, 5 and 7 were produced from Rayonier Q-LD wood pulp which meets requirements of Grade B of Spec. MIL-C-216-B. Sample 6 was produced from Buckeye Corp sheeted cotton linters which meet requirements of Class III of Spec. MIL-C-206A. Samples 8 and 9 were prepared at Defence Research Establishment Valcartier (DREV) by blending samples 7 and 4, obtained from EXPRO, respectively in a proportion 2:1 (sample 8) and 1:3 (sample 9). Samples 10 and 11 were produced at Radford Army Ammunition Plant in Virginia, U.S.A. All the Pyro, HG and Blend NC samples meet the U.S.

TABLE I

The characterized NC samples

Sample	Supplier	Cellulose source	%N	Description
1	AUSTRALIA	Wood	12.20	Displacement nitrated (1968), pine pulp
2		Cotton	12.74	Mechanically nitrated (1974), papered cotton linters
3		Wood	12.60	Mechanically nitrated (1974), a cellulose board
4	EXPRO CHEMICAL PRODUCTS (CANADA)	Wood	12.60	Pyro (lot A-1-42), Grade "A"
5		Wood	13.42	HG (from charge 2692), Grade "B"
6		Cotton	13.14	Military Blend, Grade "C", Type I, from blend # C(1) 792-L
7		Wood	13.43	HG (from charge 4712), Grade "B"
8		Wood	13.15	Blend (2/3 sample 7 + 1/3 sample 4)
9		Wood	12.80	Blend (1/4 sample 7 + 3/4 sample 4)
10	RADFORD PLANT VIRGINIA U.S.A.	Cotton	12.60	Pyro (lot RAD PE 611-23), Grade "A", Type I
11		Cotton	13.50	HG (lot RAD PE 611-24), Grade "B"
12	HERCULES (Canada Ltd)	Wood	12.0± 0.2	RS 18-25 cps (lot 9055)
13		Wood	12.0± 0.2	RS 5-6 sec (lot 9057)
14		Wood	12.0± 0.2	RS 1000-1500 sec (lot 9060)
15		Wood	12.3± 0.1	Extra-high viscosity (lot 965)
16		Wood	11.5± 0.2	AS 3-6 sec (lot 9062)
17		Wood	11.0± 0.2	SS 40-60 sec (lot 9054)

Military Specifications (MIL-N-244A). Samples 12, 13, 14, 15, 16 and 17 are industrial NC samples obtained from Hercules Canada Ltd in Toronto.

The solution properties of the NC samples are listed in Table II. The intrinsic viscosity  $[\eta]$  values were determined at 25°C in acetone and the weight average molecular weight ( $M_w$ ) values obtained from gel permeation chromatography (GPC) were determined using the NC calibration curve as described in Ref. 7. The  $M_w$  values obtained by low-angle laser light scattering (LALLS) were determined through contracts (Refs. 8 and 9). The  $M_w$  values obtained from LALLS measurements are close to those obtained by GPC except for samples 15 and 17 which had a relatively high microgel content.

## 2.2 Instrument Used

Viscosity measurements were determined at 20°C using a Haake ROTOVISKO Rotational Viscometer (Instrument #69-501). The viscometer was calibrated by using a standard liquid with the SV-I measuring system and at shear rates ranging from 3.3 to 529 s<sup>-1</sup>. The viscosity ( $\eta$ ), shear rate (G) and shear stress (P) were obtained respectively from the following relations:

$$\eta = AUS \quad (\text{cP})$$

$$G = \frac{529}{U} \quad (\text{s}^{-1})$$

$$P = \frac{G\eta}{1000} \quad (\text{Pa})$$

where

U = speed factor

S = scale reading

A = calibration constant.

### 2.3 Solutions Studied

The cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) used was obtained from Fisher Scientific Company. The CC in a 1.2 wt-% acetone solution was added to the NC also in an acetone solution. The CC weight fraction relative to NC (X) varied between 0.2 to 18 wt-%. The NC concentration (C) in the mixture was between 1.2 and 4.2 wt-% depending on the X value and the sample studied. X is related to C by the expression  $X = \frac{m}{C+m}$  where m is the CC concentration in wt-%. The value of C was chosen in such a way to allow viscosity determination with a good precision and for at least 5-7 h before gel formation because a low value for C will yield viscosity measurements lacking precision, whereas a high C value will produce a rapid gelation.

TABLE II

Solution properties of the NC samples

Sample	[ $\eta$ ] acetone dL/g	$M_w 10^{-5}$	
		GPC	LALLS+
1	3.20	2.10	1.76
2	3.00	2.50	2.11
3	3.50	2.20	1.86
4	4.50	2.70	2.34
5	3.40	2.70	
6	3.25	2.00	
7	2.83	1.90	
8	3.40	2.20	
9	3.88	2.50	
10	3.40	2.00	
11	4.00	2.10	
12	0.40	0.22	0.28
13	1.41	0.77	0.70
14	4.00	2.75	3.12
15	10.60	3.80	8.46
16	1.30	0.73	
17	1.60	1.10	1.81

+ From Refs. 8 and 9

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Cupric Chloride Effect on the Solution Viscosity

The addition of CC to the NC solution causes an increase of the viscosity as a function of time as is shown in Fig. 1 where  $\log \eta/\eta_0$  is plotted against time (t) for sample 2.  $\eta$  and  $\eta_0$  are respectively the viscosity at time t and at t = 0. This increase of the solution viscosity is probably due to the cross-linking reaction or chelate formation between CC and the nitrate groups or the residual hydroxyl groups or both. The increase of viscosity that occurs leads to the formation of complexes which is followed after a certain time by gelation. This phenomenon will be discussed in Section 3.3.

All the NC samples studied yielded complexes with the addition of CC, except sample 12 which had the lowest  $M_w$  (22,000) indicating that the complexes begin to form only when the molecular weight exceeds a certain critical value.

As shown in Fig. 1, the graph of  $\log \eta/\eta_0$  vs t yields two straight lines, each with a distinct slope. All the NC samples studied presented this common behaviour. If we assume that the rate of complex formation is proportional to the increase of viscosity with time (represented by the slope), then the complex formation between CC and NC is probably accomplished in two stages, each with a specific reaction velocity and rate constant. The first stage has a rate constant proportional to the initial slope ( $k_i$ ) and the second stage has a rate constant proportional to the final slope ( $k_f$ ):

$$k_i = \frac{d \log \eta/\eta_0}{dt} \text{ initial}$$

$$k_f = \frac{d \log \eta/\eta_0}{dt} \text{ final.}$$

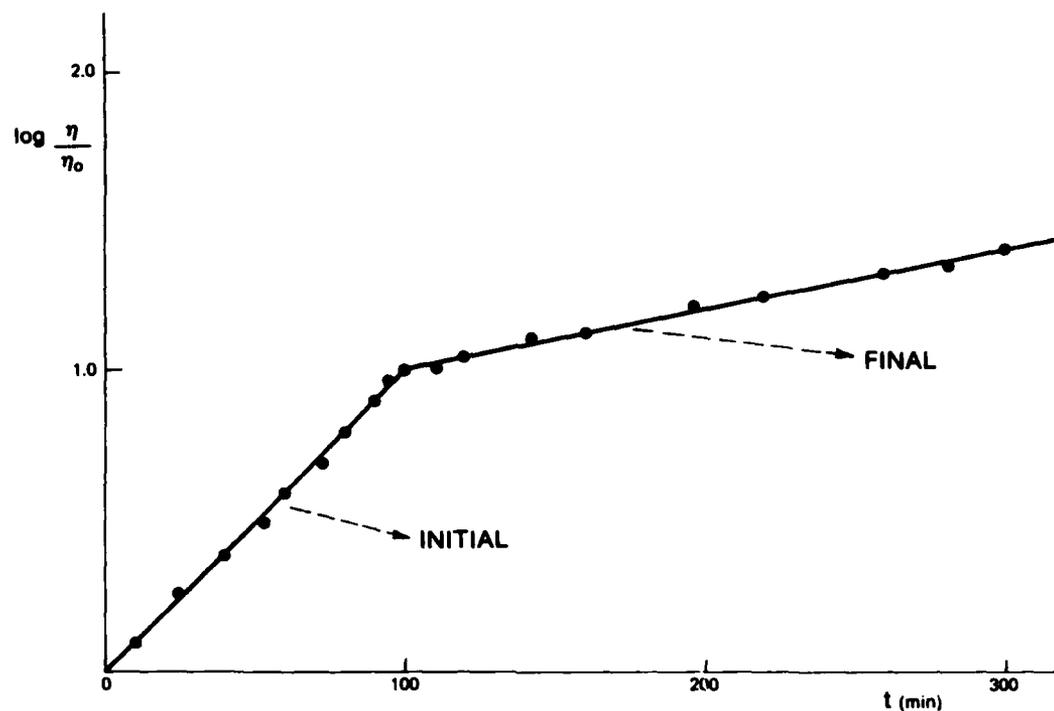


FIGURE 1 - Variation of viscosity with time for sample 2 at  $X = 6.0\%$ ,  
 $C = 2.6\%$ ,  $G = 59 \text{ s}^{-1}$

TABLE III

Effect of  $C$  on the rate of complex formation for sample 8  
 at  $X = 7.7\%$  and  $G = 59 \text{ s}^{-1}$

$C$ (%)	$k_i 10^3$ ( $\text{min}^{-1}$ )	$k_f 10^3$ ( $\text{min}^{-1}$ )	$(k_i/k_f)$
1.80	4.9	0.9	5.3
2.42	6.1	1.2	5.1
2.80	7.7	1.4	5.3
3.16	11.3	2.0	5.7

The  $(k_1/k_f)$  value represents actually the ratio of the initial stage rate constant to the final stage rate constant. In most cases  $k_1$  is higher than  $k_f$  and the ratio  $(k_1/k_f)$  depends on the NC sample studied and the chosen X value as will be shown in the next sections.

### 3.2 Effect of NC Concentration on the Rate of Complex Formation

The values of  $k_1$  and  $k_f$  as well as the ratio  $(k_1/k_f)$  obtained for sample 8 at  $X = 7.7\%$  and  $G = 59 \text{ s}^{-1}$  are reported in Table III for four different C values. The values of  $k_1$  and  $k_f$  increase with C but the ratio  $(k_1/k_f)$  for a given X value is constant ( $5.4 \pm 5\%$ ) and independent of the NC concentration in the mixture. For this reason, the ratio  $(k_1/k_f)$  will be used particularly for comparison purposes among different NC samples.

### 3.3 The Gel Point

In the course of complex formation between NC and CC, the gel point occurs at a defined stage when the mixture transforms from a viscous solution to a gel and the viscosity measurements become no longer possible. The time at which this phenomenon happens is the gelling time ( $t_{\text{gel}}$ ) which is reported in Table IV for four NC samples and at different C and X values. We notice that  $t_{\text{gel}}$  varies with the proportions of reactants as well as with the  $[\eta]$  value according to the empirical relation:

$$[\eta]^{1/2} X^{1/2} C^2 t_{\text{gel}} = 1.15 \times 10^5 \pm 15\% \text{ min ml}^{1/2} \text{ g}^{-1/2}$$

This relation was computed from the experimental results and holds for the four NC samples as shown in Table IV.

TABLE IV

Effect of C and X on the gelling time for  
different NC samples

Sample	$[\eta]$ (dL/g)	C (%)	X (%)	$t_{gel}$ (min)	$(X^{1/2}[\eta]^{1/2} C^2 t_{gel})10^{-5}$ (min mL <sup>1/2</sup> g <sup>-1/2</sup> )
15	10.60	2.46	1.5	460	1.1
		2.46	3.0	300	1.0
		2.46	5.9	210	1.0
8	3.40	3.54	4.1	255	1.2
		3.03	5.9	320	1.3
		2.42	8.0	430	1.3
17	1.60	3.43	6.2	325	1.2
		3.43	11.3	265	1.3
		3.05	13.0	310	1.3
16	1.30	4.21	8.2	190	1.1
		3.45	11.7	280	1.3
		2.63	18.2	360	1.2

TABLE V

Effect of G on the rate of complex formation  
for sample 15 at X = 5.8% and C = 1.23%

G (s <sup>-1</sup> )	$k_i 10^3$ (min <sup>-1</sup> )	$k_f 10^3$ (min <sup>-1</sup> )	$(k_i/k_f)$
3.3	11.2	0.58	19.3
10.0	7.9	0.45	17.5
59.0	6.1	0.33	18.5
265.0	4.0	0.22	18.0

As  $[\eta]$  is proportional to the NC molecular weight through the Mark-Houwink relation, we can conclude that gel formation occurs more readily when the molecular weight and the NC concentration are higher, which is in agreement with Ref. 10. It is possible of course to avoid gelation by varying the NC and CC proportions in the mixture.

### 3.4 Shear Rate Effect

The process of complex formation between NC and CC for all the samples studied followed a non-Newtonian behaviour, where the viscosity decreases with increasing shear rates as shown in Fig. 2, where  $\log \eta_G$  is plotted against  $G$  for sample 5 at  $t = 435$  min;  $\eta_G$  is the viscosity at  $G$  shear rate. It was found empirically and in the case of all the NC samples, that the graph of  $\log \eta_G$  vs  $\log \frac{1}{G+1}$ , which is also drawn in Fig. 2 for sample 5, is a straight line whose intercept yields the value of  $\eta_{G_0}$  (the viscosity at zero shear rate).

The process of complex formation between NC and CC has a pseudo-plastic flow behaviour as shown in Fig. 3, where the graph of  $P$  vs  $G$  is drawn for sample 5 at  $t = 375$  min.

The values of  $k_i$  and  $k_f$  as well as the ratio  $(k_i/k_f)$  for sample 15 for an  $X$  value of 5.8% and at four different shear rates are reported in Table V. From the results listed in this table, we notice that the values of  $k_i$  and  $k_f$  decrease with increasing shear rates, whereas the ratio  $(k_i/k_f)$  is constant ( $18.4 \pm 5\%$ ) and independent of  $G$  for a given  $X$  value. For comparison purposes, all the reported values of  $(k_i/k_f)$  were determined at  $G = 59 \text{ s}^{-1}$ .

### 3.5 Effect of $X$ on the Rate of Complex Formation

The variation of the ratio  $(k_i/k_f)$  with  $X$  is shown in Fig. 4 for sample 11 at  $G = 59 \text{ s}^{-1}$ . From the graph, we notice that the ratio  $(k_i/k_f)$  increases with  $X$  until it reaches a maximum value  $(k_i/k_f)^*$  at a

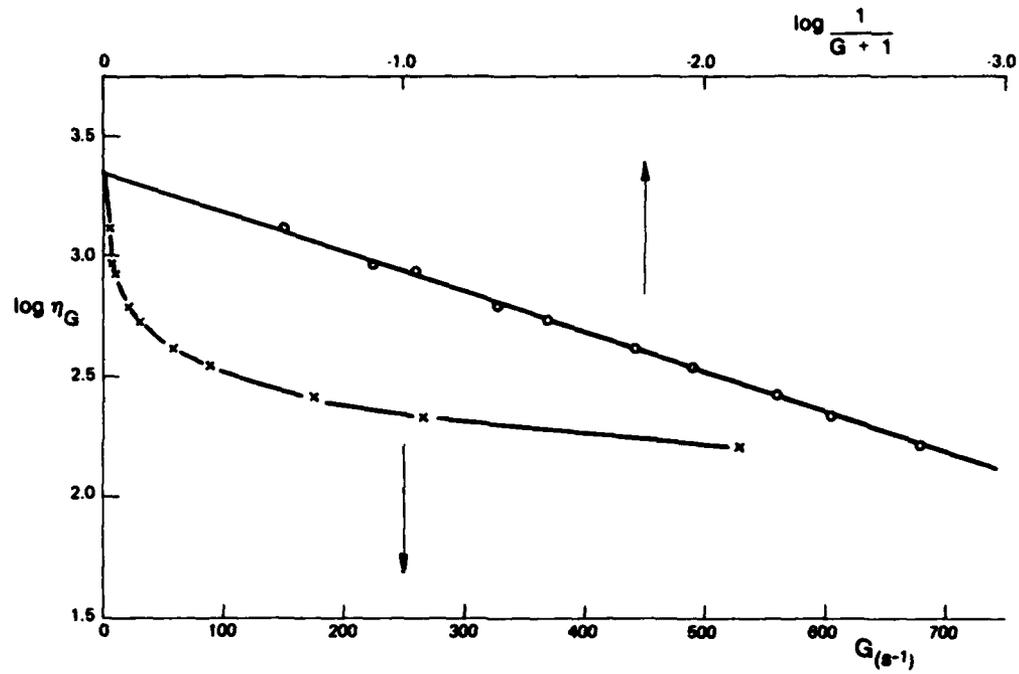


FIGURE 2 - Variation of viscosity with shear rate for sample 5  
( $t = 435$  min,  $X = 1.7\%$ ,  $C = 2.3\%$ )

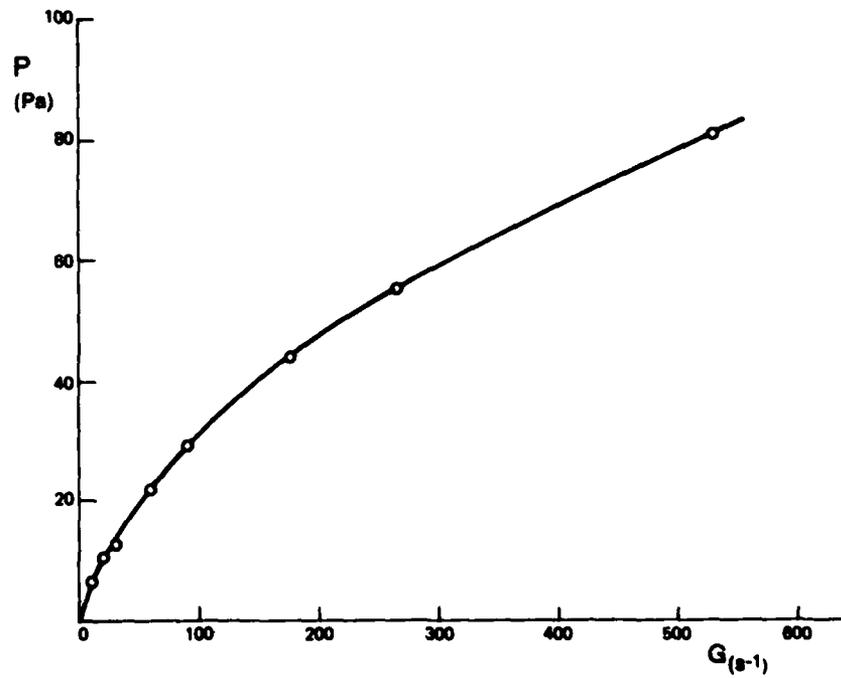


FIGURE 3 - Variation of  $P$  with  $G$  for sample 5 ( $t = 375$  min,  $X = 1.7\%$ ,  
 $C = 2.3\%$ )

certain critical value  $X^*$  (the saturation point) and then starts to decrease. All the NC samples studied presented this common behaviour. These values of  $X^*$  and  $(k_i/k_f)^*$ , obtained at the saturation point, are characteristic of the NC sample studied and are related to the polymer structure, molecular weight, nitrogen content and cellulose origin as will be shown in the next sections. The values of  $X^*$  and  $(k_i/k_f)^*$  obtained for all the NC samples studied are listed in Table VI. The asterisk designates the results obtained at the saturation point.

### 3.6 Structure Effect

In this report, the word "structure" refers to the distribution of the nitrate and residual hydroxyl groups along the polymer chains. In order to study the structure effect on the rate of complex formation, we compared the data of NC samples produced from the same cellulose source and with similar nitrogen content and  $[\eta]$  values. In this study, we chose the  $[\eta]$  rather than the molecular weight (M) because the K and a parameters in the Mark-Houwink relation  $[\eta] = KM^a$  are also related to the structure (Refs. 11 and 12).

The results obtained at the saturation point for four wood NC samples are reported in Table VII. We notice that  $X^*$  decreases with  $(k_i/k_f)^*$  from a value of 9.0 (sample 1) to a value of 3.0 (sample 4). According to these experimental results, the value of  $(k_i/k_f)^*$  is directly proportional to  $X^{*1/2}$  as indicated in Table VII, where the ratio  $\frac{(k_i/k_f)^*}{X^{*1/2}}$  has a constant value ( $3.0 \pm 10\%$ ) for all the four NC samples. Although all these samples are wood NC with approximately the same  $\bar{X}_N$  ( $12.3 \pm 0.3$ ) and  $[\eta]$  values ( $3.8 \pm 0.6$  dL/g), they present different structures as shown by their different  $X^*$  values. As CC probably forms complexes with the nitrate or unesterified hydroxyl groups or both, then the distribution of these functional groups around

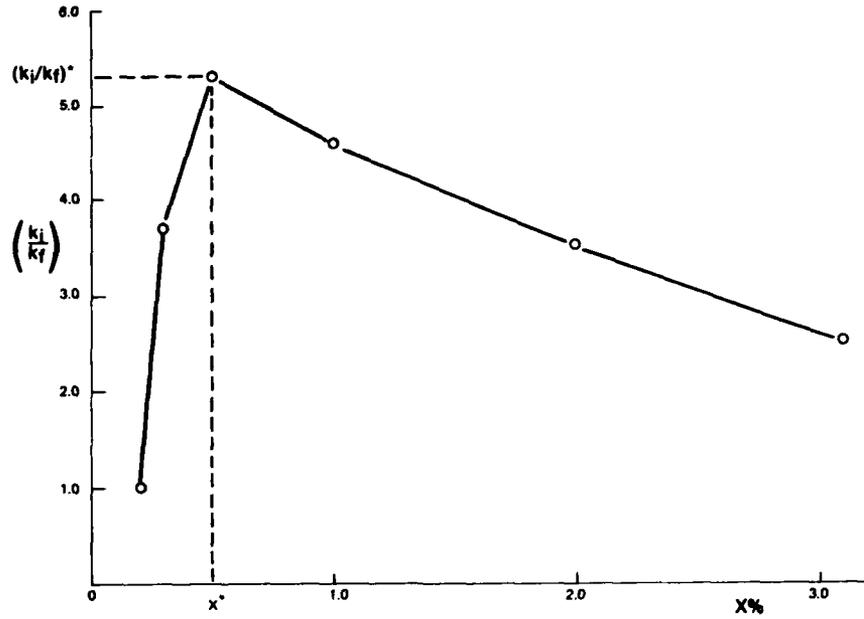


FIGURE 4 - Variation of  $(k_i/k_f)$  with X for sample 11

TABLE VI

The results obtained at the saturation point  
for the NC samples

Sample	$X^*$ (%)	$(k_i/k_f)^*$
1	9.0	7.8
2	4.5	7.4
3	6.2	7.8
4	3.0	5.7
5	1.4	8.8
6	1.9	7.0
7	2.1	7.1
8	7.7	5.7
9	2.1	5.0
10	7.6	5.6
11	0.5	5.3
12	--	--
13	11.8	2.9
14	5.0	6.8
15	5.8	18.5
16	8.4	3.4
17	11.3	4.8

the glucose units and along the cellulose chains varies from one NC sample to the other. The value of  $\bar{X}^{*1/2}$  can then be used as a structural parameter to differentiate between NC samples with similar molecular weights and degrees of nitration. We hope that the  $\bar{X}^{*1/2}$  value could be used in a simple test to distinguish between NC samples which meet all the military specifications but nevertheless yield gun propellants with different ballistic properties.

TABLE VII

Effect of structure on the rate of complex formation

Sample	$\bar{X}^*$ (%)	$(k_i/k_f)^*$	$\frac{(k_i/k_f)^*}{\bar{X}^{*1/2}}$
1	9.0	7.8	2.6
3	6.2	7.8	3.1
14	5.0	6.8	3.0
4	3.0	5.7	3.3

### 3.7 Molecular Weight Effect

In order to study the molecular weight effect on the rate of complex formation, we compared the data of NC samples with the same cellulose source and nitrogen content but with different  $[\eta]$  values. The results obtained for four wood NC samples are reported in Table VIII along with the values of  $\frac{(k_i/k_f)^*}{\bar{X}^{*1/2}}$  which take into account structural differences among the samples.

From the results listed in Table VIII, we notice that  $[\eta]$  increases with the ratio  $\frac{(k_i/k_f)^*}{\bar{X}^{*1/2}}$  whilst the ratio  $\frac{(k_i/k_f)^*}{[\eta]^{*1/2}}$  is nearly constant ( $0.70 \pm 15\%$  g/dL) for all the four NC samples. This ratio

$\frac{(k_1/k_f)^*}{[\eta]^{*1/2}}$ , denoted the "Cupric Chloride Parameter" (CCP), is an empirical factor characteristic of the NC sample as will be shown in the next section.

TABLE VIII

Molecular weight effect on the rate of complex formation

Sample	$[\eta]$ (dL/g)	$\frac{(k_1/k_f)^*}{X^{1/2}}$	$\frac{(k_1/k_f)^*}{[\eta] X^{1/2}}$ (g/dL)
15	10.60	7.70	0.73
14	4.00	3.00	0.75
1	3.20	2.60	0.81
13	1.41	0.84	0.60

3.8 Effect of Nitrogen Content and Cellulose Origin

The CCP values computed from the experimental data for all the NC samples studied are reported in Table IX. We notice that the CCP value is constant ( $0.77 \pm 20\%$  g/dL) for all the wood and cotton NC samples with %N below 12.7. Although these samples were obtained from different suppliers and had a nitrogen content between 11 and 12.6%, their CCP value was independent of the cellulose origin and the degree of nitration. However, for cotton NC samples, the CCP value increases with the degree of nitration as shown in Table IX, where the CCP value varies from 0.60 g/dL (%N = 12.6) to 1.85 g/dL (%N = 13.5). This change in the NC properties, which occurs at approximately 12.7%N, was reported by other authors who investigated this phenomenon using other techniques such as viscosimetry (Ref. 13), IR spectroscopy (Ref. 14) and X-ray diffraction (Ref. 15). The variation in the CCP value observed for cotton NC at 12.7%N, which corresponds to a degree of substitution of 2.5, results probably from the change in NC properties

occurring at the transition from dinitrate to trinitrate. No change in the CCP value was observed in the case of wood NC samples with %N below 13.4. Both wood and cotton NC of the High Grade type presented a common behaviour as shown in Table IV, where the CCP values reported for sample 5 (2.21 g/dL) and sample 7 (1.73 g/dL) are close to the one obtained for sample 11 (1.85 g/dL).

TABLE IX

Effect of %N and cellulose source on the CCP

Sample	%N	Cellulose source	CCP (g/dL)	
17	11.00	Wood	0.89	
16	11.50		0.90	
13	12.00		0.60	
14	12.00		0.75	
1	12.20		0.81	
15	12.30		0.73	
3	12.60		0.89	
4	12.60		0.73	
9	12.80		0.89	
8	13.15		0.60	
5	13.42		2.21	
7	13.43		1.73	
10	12.60		Cotton	0.60
2	12.74			1.16
6	13.14	1.60		
11	13.50	1.85		

#### 4.0 CONCLUSIONS

The process of complex formation between NC and CC in an acetone solution is accomplished in two distinct stages (initial and final), each with a specific rate constant. The ratio of the initial stage

rate constant to the final stage rate constant is independent of G and C but depends rather on the NC sample and the chosen X value.

The ratio  $(k_1/k_f)^*$  and the corresponding  $X^*$  value, obtained at the saturation (critical) point, yield valuable information on some important properties of the characterized NC sample such as the structure and the cellulose source (wood or cotton).

An empirical factor (CCP), which is specific and characteristic of the NC sample, is computed from the critical values of  $X^*$  and  $(k_1/k_f)^*$  obtained at the saturation point as well as from the  $[\eta]$  value of the polymer. Wood and cotton NC have a common CCP value for samples of the HG type ( $\%N = 13.5$ ). The CCP value can be useful to differentiate between wood and cotton NC samples mainly in the range  $12.6 < \%N < 13.4$ . In this range, the CCP value is constant for wood NC whilst it increases with the degree of nitration in the case of cotton NC.

The  $\bar{X}^{*1/2}$  value is a structural parameter that can be used in a simple routine test to distinguish between NC samples with similar molecular weight and nitrogen content. We hope that this test will be applied by Canadian industry through a research contract in order to differentiate between NC samples which meet all the military specifications but yield gun propellants with different ballistic properties. It is very important for Canadian industry to define some physical and chemical properties of wood and cotton NC to identify those properties responsible for the variations in ballistic performance in order to allow the specification of NC by reference to these properties rather than to cellulose origin.

From the results obtained in this study, we cannot conclude whether the nitrate or the residual hydroxyl groups of NC were directly involved in the process of complex formation with CC. To clarify this

point, other techniques such as nuclear magnetic resonance should be investigated.

#### 5.0 ACKNOWLEDGEMENTS

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