

AD-A009 506

STUDY OF THE REACTION OF CELLULOSE  
NITRATE WITH ISOCYANATES

Jack Bobinski

Picatinny Arsenal  
Dover, New Jersey

March 1975

DISTRIBUTED BY:

**NTIS**

National Technical Information Service  
U. S. DEPARTMENT OF COMMERCE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER Technical Report 4718	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD. ACC 9.506	
4. TITLE (and Subtitle) STUDY OF THE REACTION OF CELLULOSE NITRATE WITH ISOCYANATES		5. TYPE OF REPORT & PERIOD COVERED	
7. AUTHOR(s) Jack Bobinski		6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Propellants Division, FRL Picatinny Arsenal Dover, New Jersey 07801		8. CONTRACT OR GRANT NUMBER(s) DA Project 1T061102A32C-01 AMCMS Code 611102.11.85701	
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE March 1975	
		13. NUMBER OF PAGES 40	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release, distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Nitrocellulose Phenyl isocyanate Cellulose nitrate phenyl carbamate Cellulose nitrate			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Cellulose nitrate phenyl carbamate was synthesized and characterized. When studying the synthesis, it was discovered that it is not necessary to conduct this reaction under strictly anhydrous conditions. The reaction is aided by the excess of phenyl isocyanate, elevated temperatures, suitable solvents and a low degree of substitution of nitrocellulose. Denitration occurs as the reaction progresses; however, the formation of the carbamate substituent is not directly related to the loss of the nitrate groups.			

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U.S. Department of Commerce  
Springfield, VA 22151

PRICES SUBJECT TO CHANGE

The citation in this report of the names of commercial firms or commercially available products or services does not constitute official endorsement or approval of such commercial firms, products, or services by the US Government.

## ACKNOWLEDGMENT

The author wishes to thank Mr. Nathaniel Gelber and Mr. Edward Turngren for their assistance in the characterization of the synthesized compounds.

## TABLE OF CONTENTS

	Page No.
Introduction	1
Results and Discussion	2
Validation of Experimental Results	2
Reaction Time as a Variable in Reaction Study	3
Nitrocellulose, 13.88%N (DS 2.90) Starting Material	3
Reaction of Nitrocellulose With Tollyl Isocyanate Isomers	4
Effect of Concentration of Phenyl Isocyanate Upon the Urethane Substitution	5
Effect of Total DS Upon Further Substitution	6
Effect of Water Upon the Reaction	7
Effect of Dilution Upon the Reaction	7
Effect of Excess Isocyanate Upon the Reaction	8
Effect of Catalysts Upon the Reaction	8
Effect of Temperature Upon the Reaction	10
Heat Stability of Cellulose Nitrate Phenyl Carbamate	10
Experimental Procedures	11
Reagents	11
Reaction of Nitrocellulose With Phenyl Isocyanate	11
Reaction of Nitrocellulose With Phenyl Isocyanate Under Anhydrous Conditions	12
Impact Sensitivity Test	12
Temperature of Explosion Test	12
Heat Stability Test	12
Determination of Nitrogen	13
Conclusions	13
Recommendation	14
References	15
Distribution List	34
Tables	
1 Reaction time as the variable in the reaction of nitrocellulose with phenyl isocyanate at 69°C, in tetrahydrofuran, for 5 hr	16

## Tables

2	Reaction of nitrocellulose DS 2.44 and DS 2.90 with phenyl isocyanate at 69°C, in tetrahydrofuran	17
3	Reaction of nitrocellulose with o-tolyl isocyanate in cyclohexanone, at 110°C	18
4	Reaction of nitrocellulose with m-tolyl isocyanate in cyclohexanone, at 110°C	19
5	Reaction of nitrocellulose with p-tolyl isocyanate in cyclohexanone, at 110°C	20
6	Reaction of nitrocellulose with tolyl isocyanate isomers	21
7	Reaction of nitrocellulose with p-tolyl isocyanate at 69°C and at 110°C	22
8	Effect of phenyl isocyanate upon cellulose nitrate phenyl carbamate 69°C, 5 hrs, in tetrahydrofuran	23
9	Changes in DS of nitrocellulose and cellulose nitrate phenyl urethane under varied conditions	24
10	Effect of water upon the reaction of 0.01 mole of nitrocellulose with excess of phenyl isocyanate at 69°C, in tetrahydrofuran	25
11	Effect of dilution upon the reaction of 0.01 mole of nitrocellulose with excess of phenyl isocyanate at 69°C, in tetrahydrofuran, for 5 hr	26
12	Effect of excess of phenyl isocyanate reacted with 0.01 mole of nitrocellulose at 69°C, in tetrahydrofuran, for 5 hr	27
13	Effect of stannous octoate catalyst upon the reaction of nitrocellulose with excess of phenyl isocyanate at 69°C, in tetrahydrofuran, for 5 hr	28

## Tables

14	Effect of various catalysts upon the reaction of nitrocellulose with phenyl isocyanate at 69°C, in tetrahydrofuran, for 5 hr	29
15	Effect of temperature upon the reaction of nitrocellulose with phenyl isocyanate in 1,4-dioxane, for 5 hr	30
16	Stability of cellulose nitrate phenyl carbamate DS 2.10-ONO <sub>2</sub> - 0.54 ØNCO and nitrocellulose 12.57%N	31

## Figures

1	Degree of substitution of phenyl carbamate vs reaction time - no catalyst	32
2	Degree of substitution of phenyl carbamate vs reactime time - stannous octoate catalyst	33

## INTRODUCTION

Nitrocellulose has been studied extensively with regard to its synthesis, thermal and explosive properties, degree of polymerization and other similar aspects. However, the literature contains relatively little mention of studies on the synthesis and the characteristics of compounds that are obtained by chemical modification of nitrocellulose.

Isocyanates react readily with hydroxy compounds to form stable carbamate. The synthesis of cellulose nitrate carbamates appeared promising. This type of study seemed to be particularly attractive when approached by using the synthesis of cellulose nitrate carbamates by the reaction of nitrocellulose with isocyanates and the nitration of cellulose carbamate intermediates. The fact that the study was related to crosslinking of propellants was also significant.

A literature search disclosed that a U.S. patent (Ref 1) issued in 1954 mentioned the reaction of nitrocellulose with isocyanates, however it contained no information as to the synthesis and properties of the proposed compound.

In 1970, Freidgein et al (Ref 2), suggested using nitrocellulose modified by urethane polymers as leather substitutes. The literature search did not otherwise show any systematic investigation in this area of chemistry.

At the onset of the study of the reaction of nitrocellulose with isocyanates, the objective was to prove the feasibility of this reaction. Military grade nitrocellulose and phenyl isocyanate were selected for their high reactivity and availability. The reaction was studied in suitable solvents which dissolved or gelled the reaction mixture. The products structure and substitution were determined on the basis of infrared absorption spectra, nitrate and total nitrogen analysis. Depending on the reaction conditions, the products had varied degrees of substitution of the nitrate and phenyl carbamate groups. At elevated temperatures and over a prolonged period of time, it was observed that the trimer of phenyl isocyanate (triphenyl isocyanurate) was formed. The trimer was isolated and identified on the basis of the elemental analysis and its melting point of 285°C. Triphenyl isocyanurate was effectively separated from the reaction product by a mixture of tetrahydrofuran and cyclohexane.

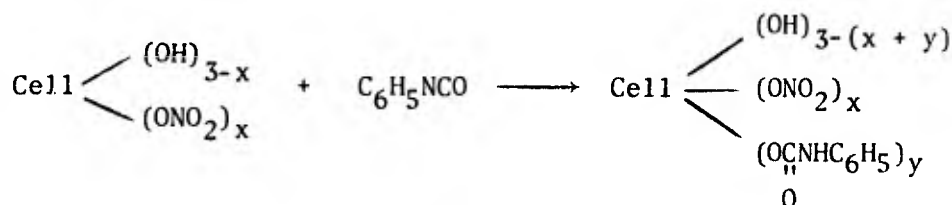


## RESULTS AND DISCUSSION

Cellulose nitrate phenyl carbamate was synthesized by the reaction of nitrocellulose, 12.63% nitrogen DS 2.44, with phenyl isocyanate in a small amount of tetrahydrofuran at 69°C, the boiling point of the reaction mixture. For the 0.01 mole of nitrocellulose, 20 ml of tetrahydrofuran were used. The quantity of tetrahydrofuran was determined experimentally in order to use just enough of the solvent to gel the nitrocellulose. After heating to 69°C the reaction mixture became homogeneous and was agitated with a magnetic bar.

Purification of the reaction product was accomplished by diluting the reaction mixture in tetrahydrofuran with the addition of acetone. The resulting solution was poured into cyclohexane. Then the product, separated as a firm gel, was dissolved in acetone and the resulting solution poured slowly with stirring into a large volume of water to bring about a fibrous material. Finally, the product was treated in a Waring Blendor isolated and dried under environmental conditions and then under reduced pressure at 55°C. The structures of the products were determined on the basis of nitrate nitrogen and total nitrogen analyses. Infrared absorption spectra were used to verify the proposed structures.

The reaction of nitrocellulose with phenyl isocyanate may be illustrated as follows:



### Validation of Experimental Results (Table 9)

During the process of the interaction of nitrocellulose with phenyl isocyanate, partial denitration occurred. The possibility of the interdependence of these two mechanisms, the formation of the carbamate on one hand and loss of the nitrate groups by nitrocellulose on the other, was considered. It was obvious that this was not just a replacement reaction of the nitrate by the carbamate groups, because the original DS of 2.44 could have been increased to DS 2.71, the total substitution in the product. A high degree of validity and reproducibility of the analytical results excluded the possibility

that unreliable data had accounted for the total DS of the product being 0.27 higher than the DS of the nitrocellulose.

In order to validate the experimental findings, it was necessary to evaluate the effect of the heating of nitrocellulose in tetrahydrofuran without phenyl isocyanate and isolating and purifying of the product.

When this was accomplished, the nitrate and total nitrogen analysis showed that the original nitrocellulose DS 2.44, after heating in tetrahydrofuran for 48 hours at 69°C, contained 2.38 nitrate groups per anhydroglucose.

#### Reaction Time as a Variable in Reaction Study

A series of reactions of military grade nitrocellulose with phenyl isocyanate was conducted in which the reaction time allowed was the only variable. A longer interaction of the reagents at 69°C was associated with an increasingly greater degree of phenyl carbamate substitution and a higher degree of denitration. Table 1 presents these results.

Utilizing the data of Table 1, Figure 1 was constructed to illustrate the relationship of the degree of substitution of phenyl carbamate to the reaction time. As the curve shows, at the beginning of the reaction, there was a rapid increase in the phenyl carbamate substitution. Then, after several hours, the reaction leveled off. In fact, within the first three hours of the reaction the increase in the total degree of substitution was practically as large as that during the following 117 hours. After 120 hours reaction time, the product, cellulose nitrate phenyl carbamate, contained 2.05 nitrate and 0.63 phenyl carbamate groups, total DS 2.68 (compared to 2.44, the degree of substitution of nitrocellulose the starting material).

The reaction was conducted in a homogeneous medium with a large excess of phenyl isocyanate. In spite of this, complete substitution of the nitrocellulose, DS 3, was not reached. It is hoped that this occurrence would be clarified in a further study of the reaction.

#### Nitrocellulose, 13.88%N (DS 2.90) Starting Material

The reaction of nitrocellulose, DS 2.44, with phenyl isocyanate, conducted under a variety of conditions, produced cellulose nitrate phenyl carbamate containing a maximal total DS of 2.71 by the nitrate and the carbamate groups. In view of this finding, it was plausible to hypothesize that the steric factor was responsible for the incomplete substitution of the products. To clarify this possibility,

an attempt was made to react a highly substituted nitrocellulose, DS 2.90, with phenyl isocyanate under previously investigated reaction conditions.

As Table 2 shows, after five hours of interaction, the nitrogen analysis of the product showed a negligible carbamate substitution. In this case a possibility existed that since the DS 2.90 nitrocellulose happened to have a relatively high degree of polymerization, a lower concentration of the polymer in solution might enhance the reaction. Therefore, in the next experiment, the quantity of the solvent was increased to give a solution of 0.005 mole of nitrocellulose in 40 ml of tetrahydrofuran. This time, after five hours reaction of 69°C, the product was found to contain 2.79 nitrate and 0.03 phenyl carbamate groups per anhydroglucose.

Owing to a higher dilution of nitrocellulose, the reaction did occur and the product had a total substitution of 2.82 as compared to the previously obtained highest total DS of 2.71. However, when comparing these two reactions, it is necessary to take under consideration the relative degrees of the nitrate and the carbamate substitution in each product, as this may be a contributing factor affecting the total substitution.

In the reaction, in which the product had the total DS of 2.82, the DS of the starting material was 2.90, 0.08 higher than the DS of the product. Highly substituted nitrocellulose loses nitrate groups fairly easily. In the reaction under discussion, the occurred loss was not compensated by the urethane substitution.

#### Reaction of Nitrocellulose With TolyI Isocyanate Isomers

The effect of the methyl substituent upon the reaction of phenyl isocyanate with nitrocellulose was investigated. This study is related to the reaction of nitrocellulose with tolylene-2,4-diisocyanate a crosslinking agent used in propellant formulations. In a series of experiments, nitrocellulose, DS 2.44, was reacted with ortho, meta and para tolyl isocyanate at 110°C, in cyclohexanone. The reaction times were: one, three, five and seven hours. The experimentally obtained results are shown in Tables 3, 4, 5, and 6.

It was found that p-tolyI isocyanate was the most reactive and o-tolyI isocyanate the least reactive towards the unsubstituted hydroxyl groups of nitrocellulose. For example, after seven hours of reaction time, cellulose nitrate p-tolyI carbamate contained 1.71 nitrate and 0.77 carbamate groups per anhydroglucose. The DS of cellulose nitrate o-tolyI carbamate was 1.80 nitrate and 0.48 carbamate groups.

In an attempt to obtain a product with a high degree of total substitution, the synthesized cellulose nitrate p-tolyl carbamate, DS 1.77  $-\text{ONO}_2$  and 0.77 carbamate groups, was reacted with p-tolyl isocyanate. The reaction was conducted in tetrahydrofuran at  $69^\circ\text{C}$ . A relatively low reaction temperature was selected to minimize the denitration of the polymer. After five hours of reaction the substitution of p-tolyl carbamate in the cellulose nitrate p-tolyl carbamate increased slightly from 0.77 to 0.85 per anhydroglucose. The total substitution of the product was 2.72, leaving 0.28 unsubstituted hydroxyl groups of the compound.

A series of reactions of nitrocellulose with p-tolyl isocyanate at  $69^\circ\text{C}$  and  $110^\circ\text{C}$ , with the reaction time varied from one to seven hours, showed that the differences in the total substitution of the products were slight. However, as Table 7 illustrates, the substitution of the products by the carbamate was associated with a considerably higher degree of denitration at the higher temperature. Since denitration of nitrocellulose produces  $\text{NO}_2$  gas, porosity of the body of the propellant containing tolylene-2,4-diisocyanate crosslinking agent would be expected to increase with a higher curing temperature.

#### Effect of Concentration of Phenyl Isocyanate Upon the Urethane Substitution

To find out the effect of a concentration of phenyl carbamate upon the total degree of substitution in the product, the following experiment was carried out. Cellulose nitrate phenyl carbamate was obtained after 42 hours of reaction of nitrocellulose with phenyl isocyanate. It was purified, and then reacted with phenyl isocyanate. Both reactions were conducted under the same conditions. The interaction of cellulose nitrate phenyl carbamate with phenyl isocyanate brought about a negligible increase of the phenyl carbamate groups, from 0.54 to 0.58, and a loss of the nitrate groups ( $-\text{ONO}_2$  substitution) from 2.10 to 1.93.

On the basis of these results, it may be concluded that under the reaction conditions, the concentration of the reagents in the first reaction was not responsible for incomplete substitution.

The formation of the phenyl carbamate substituent is not directly related to the loss of the nitrate groups. Since the original total DS of 2.44 in nitrocellulose was increased in some products to DS 2.70, some of the free hydroxy groups in the starting material must have reacted with the phenyl isocyanate.

The effect of the presence of phenyl isocyanate upon cellulose nitrate phenyl isocyanate was further investigated. The experimental results of this investigation are shown in Table 8. They were obtained by reacting nitrocellulose at 69°C for five hours in tetrahydrofuran with phenyl isocyanate. The product of this reaction was isolated and purified and reacted again with phenyl isocyanate at 69°C for five hours in tetrahydrofuran. This operation was repeated three times and resulted in obtaining four samples of the products that differed from each other in regard to the number of times they had been reacted with phenyl isocyanate.

Table 8 shows remarkably similar structures of the products having substitution by the nitrate from 2.05 to 2.20 and the carbamate from 0.41 to 0.54. The yield of the first reaction was 88.4%. The three successive reactions gave respectively 87.4, 73.4 and 58.5 per cent yield. The successively decreasing yield may be associated with the increasing depolymerization of the cellulosic chains, followed by the loss of the low degree of polymerization fraction during isolation and purification of the products. Furthermore, the increasing loss of each successive yield may indicate that the products of the lower degree of polymerization tended to increase the rate of further depolymerization.

The product of the fourth reaction represented quantitatively 37.6% of the product obtained from the first reaction. Since these two materials were characterized by almost the same degrees of substitution by the nitrate and the carbamate groups, it was concluded that the first product was of high purity and it was uniformly substituted. Therefore high purity cellulose nitrate phenyl carbamate can be synthesized in a relatively high (88.4%) yield.

#### Effect of Total DS Upon Further Substitution

The higher the total substitution in cellulose nitrate phenyl carbamate, the more difficult it was to introduce additional phenyl isocyanate into the structure of the compound. This aspect is illustrated by two reactions conducted under the same conditions, except that nitrocellulose in one case had DS 2.44 and in another, DS 2.90. In the case of the lower substituted nitrocellulose, the product of the reaction was found to contain 0.29 phenyl carbamate groups when the higher substituted cellulose nitrate product contained only 0.03 of the corresponding carbamate substituents. The respective total degrees of substitution were 2.58 and 2.82 for each anhydroglucose.

## Effect of Water Upon the Reaction

As isocyanates react quite readily with water, anhydrous conditions are usually recommended for the isocyanate-alcohol reactions. However, it is not unreasonable to expect that a small amount of water may have a catalytic effect upon the reaction. J. H. Saunders and K. C. Frisch (Ref 3) reported that the rate of uncatalyzed reaction of phenyl isocyanate with alcohol increased with an increase in the concentration of the alcohol.

To clarify this aspect, reactions of nitrocellulose with phenyl isocyanate were conducted in the presence of 0.01 ml, 0.02 ml, 0.05 ml and 0.10 ml of water which was introduced into a solution of 0.01 mole of nitrocellulose in 20 ml of tetrahydrofuran. Table 1 illustrates these experiments. The reaction was carried out at 69°C and there was a large excess of phenyl isocyanate. The reagents were allowed to react for one hour and then the products were isolated and purified. They were found to contain the carbamate substitutions of 0.08, 0.12, 0.10, and 0.13. Then a reaction was conducted under the same conditions but without water. This time the product contained 0.05 phenyl carbamate groups per anhydroglucose. These experimental results seemed to indicate that the presence of small quantities of water had a negligible effect upon the reaction of nitrocellulose with phenyl isocyanate.

The reaction of nitrocellulose with phenyl isocyanate at 60°C, under anhydrous conditions over a period of five hours produced a compound which contained 0.33 phenyl carbamate and 2.21 nitrate groups. A repeated reaction under the same conditions but with 0.10 ml of water introduced into a 20 ml tetrahydrofuran solution of 0.01 mole of nitrocellulose resulted in formation of a product which contained 0.45 carbamate and 2.23 nitrate groups. These results indicate that with a large excess of isocyanate, a small quantity of water may tend to catalyze the reaction of nitrocellulose with phenyl isocyanate.

## Effect of Dilution Upon the Reaction

When analyzing the nitrocellulose phenyl isocyanate reaction, it may be considered that an increased amount of solvent may render the polymeric chains of nitrocellulose more accessible to interaction with the molecules of phenyl isocyanate. To clarify this hypothesis, four reactions were conducted in which for 0.01 mole of nitrocellulose, 20 ml, 40 ml, 80 ml, and 160 ml of tetrahydrofuran were used. The products of these reactions were isolated and purified in the previously described manner. As Table 11 shows, the

highest dilution (160 ml) of the solvent per 0.01 mole of nitrocellulose, produced only 0.04 carbamate substitution. The highest carbamate substitution of 0.33 was found in the product of the reaction in which 0.01 mole of nitrocellulose was dissolved in 40 ml of the solvent.

A very high dilution possibly favored accessibility of nitrocellulose molecules to those of phenyl isocyanate. At the same time, the high dilution was decreasing the chance of effective collision of the molecules of the reagents, the result of which was a relatively lower rate of formation of the carbamate bond.

#### Effect of Excess Isocyanate

Often, in order to increase the degree of substitution in cellulose derivatives, a large excess of the substituting reagent is recommended. This aspect was investigated in regard to the reaction of nitrocellulose with phenyl isocyanate. The reaction was conducted under the previously described conditions for period of five hours and is presented in Table 12.

At the molar ratio of nitrocellulose to phenyl isocyanate, (one to two respectively) the product contained 0.11 carbamate groups per anhydroglucose. Further increase of the relative ratio of phenyl isocyanate to nitrocellulose resulted in an increase of the carbamate substitution, giving the ratio of 3.8 to 1 for a product which contained 0.24 carbamate groups per anhydroglucose. Further increase in the relative ratio of phenyl isocyanate to nitrocellulose, from 3.8 to 7.4 moles, increased the DS of the carbamate groups from 0.24 to 0.29.

These observations indicate that, under the experimental conditions little advantage was achieved when the respective molar ratio of phenyl isocyanate to nitrocellulose was higher than four to one.

#### Effect of Catalysts Upon Reaction

The reaction of isocyanates with hydroxy compounds may be catalyzed by bases, the catalytic effect of which is expected to increase with the higher base strength. However, since nitrocellulose tends to decompose in the presence of bases, the use of these compounds in the nitrocellulose phenyl isocyanate reactions is limited. Since stannous octoate is known to be an effective catalyst for reactions of phenyl isocyanate with alcohols and is characterized by its low basic strength, this compound was selected for catalysis of the reaction under study.

Table 13 presents a series of nitrocellulose phenyl isocyanate reactions catalyzed by stannous octoate with the time factor as the only variable. It was found that in this reaction stannous octoate catalyzed the formation of phenyl carbamate but simultaneously it also tended to increase denitration. When no catalyst was used, loss of the  $-ONO_2$  groups in the starting material also occurred but to a lesser degree. The effect of the stannous octoate catalyst upon the reaction of nitrocellulose with phenyl isocyanate is illustrated in Figure 2.

As Figure 2 shows, the initial catalytic effect of stannous octoate upon the degree of substitution of phenyl carbamate in the product gradually decreased with time and, after about one hundred hours reaction time, became negligible.

In a further study of the catalyzed reaction of nitrocellulose with phenyl isocyanate, tetrabutyltin, tributyltin chloride, butyltin trichloride and 1,4-diazabicyclo-[2,2,2]-octane were used. The reactions were conducted in tetrahydrofuran at  $69^\circ C$ , over a period of five hours.

As Table 14 shows, the products obtained differed little with respect to their substitution by the carbamate groups. The range of the carbamate was found to be from 0.44 to 0.50 and the DS of the nitrate ranged from 2.08 to 2.19. Since this reaction, conducted without any catalyst, gave a product containing 0.29 carbamate and 2.29 nitrate groups per anhydroglucose, it may be concluded that the selected catalysts increased the carbamate substitution. The narrow range of the carbamate substitution in the reactions with various catalysts suggested that in each case an equilibrium was reached during the process of reaction regardless of the type of catalyst used. The effect of the individual catalysts upon the carbamate substitution in the products may have been more significant before the reaction time reached five hours.

Analysis of the products obtained showed that the use of the catalysts was associated with an increased degree of denitration. Among the investigated catalysts, tetrabutyltin was possibly the strongest base because it caused the greatest degree of denitration. The total degree of substitution of the combined nitrate and carbamate groups in the catalyzed reactions ranged from 2.52 to 2.68, leaving about 0.3 unsubstituted hydroxyl groups per anhydroglucose.

At this stage of the study it was considered that perhaps a catalyst of a relatively high basic strength might, in spite of its denitrating effect, produce high total substitution. Triethylamine was selected for this purpose. It was found that the



product of the reaction catalyzed by triethylamine had the total DS of only 2.61. The loss of the nitrate groups corresponded to that which occurred in the presence of 1,4-diazabicyclo-[2,2,2]-octane, the catalyst which is known to be of relatively low basic strength.

However, the yield of the product obtained from the reaction catalyzed by triethylamine was found to be 60 per cent, as compared to about 77 per cent yield observed when other catalysts were used. The lower yield from the reaction catalyzed by triethylamine may be explained by the fact that a relatively strong base causes considerable depolymerization of the polymeric cellulosic chains. This may have led to the subsequent loss of the low degree of polymerization fraction in the product during isolation and purification.

#### Effect of Temperature Upon Reaction

As in the case of p-tolyl isocyanate, the reaction of nitrocellulose with phenyl isocyanate was found to be temperature dependent. In order to investigate this aspect of the experimental conditions, the solvent, tetrahydrofuran, was replaced by 1,4-dioxane. As Table 15 shows, the increase of the reaction temperature from 70°C to 100°C, with the remaining conditions unchanged, was reflected in an increase of the carbamate substitution from 0.29 to 0.49 per anhydroglucose. The reactions were conducted over a period of five hours. Since even at 100°C the total substitution of the product was 2.61, (leaving 0.39 hydroxyl groups unsubstituted) it was of interest to conduct this reaction over an extended period of time. The increase of the reaction time from five to thirty hours resulted in the formation of the product with 1.82 nitrate and 0.59 carbamate substitution. A higher phenyl carbamate substitution in the product did not compensate for the loss of the nitrate groups, making the total DS 2.41, lower than the total DS of the product obtained after a shorter reaction time.

#### Heat Stability of Cellulose Nitrate Phenyl Carbamate

Table 16 presents the evaluation of stability for a representative sample of cellulose nitrate phenyl carbamate. The DS was 2.10 nitrate and 0.54 phenyl carbamate groups. The compound had a somewhat higher heat stability at 134.5°C than nitrocellulose (12.63% nitrogen), the starting material. However, the tested sample was found to generate 4.03 ml of gas at 100°C in a vacuum (reduced pressure) over a period of forty hours. This figure compared unfavorably to the figure of .89 ml of gas generated by the nitrocellulose under the same conditions. Therefore, an attempt was made to improve the vacuum stability of the cellulose nitrate phenyl carbamate. The

investigated product was heated in a 0.01 per cent aqueous sodium carbonate solution for one hour at 90°C, then filtered and washed with water. This operation was repeated three times. The applied stabilization procedure was highly effective because the product evolved only 0.81 ml of gas in the vacuum stability test. This amount was slightly lower than the figure 0.89 ml which characterized the vacuum stability of the nitrocellulose, the starting material.

## EXPERIMENTAL PROCEDURES

### Reagents

Poudrerie Nationale Bergerac, France, supplied nitrocellulose (13.88% nitrogen). Nitrocellulose supplied by Hercules Inc, pyro grade, lot no. 7314 (12.63% nitrogen) came from one single nitration lot. Phenyl isocyanate with a boiling point of 60-62°C/20 mm was supplied by Matheson, Coleman and Bell. Tetrahydrofuran was Baker Analyzed Reagent, purity: 99.9%, water: 0.007%.

### Reaction of Nitrocellulose With Phenyl Isocyanate

Nitrocellulose (12.63%N), 2.73g (0.010 mole) was reacted with phenyl isocyanate, 8.75g (0.074 mole), in 20 ml of tetrahydrofuran at 69°C for five hours. After cooling to room temperature, the mixture was combined with 130 ml of acetone and the resulting solution was stirred and poured into 200 ml of cyclohexane. This caused the separation of a firm gel. The gel was isolated, pressed to remove solvent, and then dissolved in 200 ml of acetone. The acetone solution was then stirred and poured gradually into three liters of water and the precipitating fibrous material was separated from the water, treated in a Waring Blendor, filtered, washed with water, and dried. The yield was 2.32g (77%). The analysis was found to be 10.71% -ONO<sub>2</sub> nitrogen and 12.06% total nitrogen which corresponded to the DS of 2.29 -ONO<sub>2</sub> and 0.29 C<sub>6</sub>H<sub>5</sub>N<sub>1</sub>C<sub>1</sub>O<sub>1</sub> groups per anhydroglucose.

The infrared absorption spectrum was in agreement with the proposed structure of cellulose nitrate phenyl carbamate.

Nitrocellulose (13.88%N), 2.91g (0.01 mole) was reacted with phenyl isocyanate, 8.75g (0.074 mole) in 80 ml of tetrahydrofuran at 69°C for five hours. After cooling to room temperature, the mixture was combined with 50 ml of acetone and the resulting solution

was stirred and poured into 200 ml of cyclohexane which caused separation of the firm gel. The gel was isolated, pressed to remove solvent, and then dissolved in 200 ml of acetone. The acetone solution was poured gradually with stirring into three liters of water and the precipitating fibrous material was separated from water, treated in a Waring Blendor, filtered, washed with water, and dried. The yield was 2.50g (86%). The analysis was found to be 13.43%  $-ONO_2$  nitrogen and 13.56% total nitrogen which corresponded to the DS of 2.79 nitrate and 0.03 phenyl carbamate groups per anhydroglucose.

#### Reaction of Nitrocellulose With Phenyl Isocyanate Under Anhydrous Conditions

Tetrahydrofuran, 35 ml containing 0.007% water, was rendered dry by azotropic distillation with 170 ml of n-pentane. The system was protected from atmospheric moisture by tubes containing drierite and by the application of protective nitrogen atmosphere during the operations. The azotropic mixture distilled at 56.0-65.5°C/atm until about 30 ml of the solvent remained in the distillation flask. Then 2.73g of dry nitrocellulose and 8 ml of phenyl isocyanate were combined with distilled tetrahydrofuran. The resulting mixture was heated at 69°C and stirred with a magnetic bar for five hours. After cooling to room temperature, the product was isolated and purified. The yield was 2.44g (81%). The analysis was found to be 10.30% nitrate nitrogen and 11.83% total nitrogen. The DS consisted of 2.21 nitrate and 0.33 phenyl carbamate groups per anhydroglucose.

#### Impact Sensitivity Test

The test was done with a Picatinny Arsenal apparatus on 5 mg quantities of sample for each trial. The procedure is described in Reference 6.

#### Temperature of Explosion Test

This procedure is described in detail in Reference 6.

#### Heat Stability Test

The heat stability test was conducted at 134.5°C following the procedure described in Reference 6.

## Determination of Nitrogen

The nitrate nitrogen was reduced under an inert atmosphere with ferrous alum in an acidified solution of butyl acetate and acetic acid. The resulting ferric ion was titrated with standard titanous chloride. One milliequivalent equals  $1/3$  millimole which equals 4.669 mg.

The Kjeldahl method for nitrate containing material was used. The sample was dissolved in a solution of salicylic acid in concentrated sulfuric acid. Potassium sulfate was added to elevate the boiling point. Mercuric oxide was added as a catalyst. The mixture was digested, then cooled and made alkaline. The resulting ammonia was distilled into boric acid and titrated with standard hydrochloric acid. One milliequivalent of nitrogen equaled one millimole which equals 14.008 mg.

## CONCLUSIONS

Cellulose nitrate phenyl carbamate, with a total degree of substitution (DS) from 2.5 to 2.6, can be easily synthesized and effectively purified. The study of this synthesis showed the effects of reaction conditions upon the denitration of nitrocellulose.

During the curing or storage of solid propellants containing nitrocellulose and diisocyanate (a cross-linking agent), cracking of the propellant grain occurred frequently. This may be caused by the denitration of nitrocellulose leading to the formation of oxides of nitrogen, which in turn would create in the grain nonuniformly distributed voids. Using the findings of this report, denitration of nitrocellulose in the presence of an isocyanate can be reduced. Consequently, it may be possible to prevent cracking of the propellant and perhaps, to also improve the uniformity of its combustion. To prevent formation of undesirable oxides of nitrogen, avoidance of high curing temperatures, avoidance of introduction of basic ingredients in formulation, and completion of the cross-linking process before storage, is suggested.

The cellulose nitrate phenyl carbamate showed resistance to ignition, as compared to nitrocellulose. This characteristic may be of interest if a safety aspect is important in some applications.

## RECOMMENDATION

An evaluation of cellulose nitrate phenyl carbamate and nitrocellulose is recommended to determine the possible advantages offered by this compound over nitrocellulose, especially when considered for use in specific military applications such as the manufacture of caseless small caliber ammunition.

## REFERENCES

1. Schnell, H. and Rinke, United States Patent 2,678,869, May 18, 1954.
2. Freidgin, K. I. et al, Kozhevenno-Obuvnaya Promyshlennost, 1970, 12(2), 41-4 (Russian).
3. Saunders, H. H. and Frisch, K. C., Polyurethanes Chemistry and Technology, Interscience Publishers, New York and London, 1962.
4. Analytical Chemistry Branch Report. No. AL-P-21-62, (April 1962).
5. Analytical Chemistry Branch Report, No. AL-P-423-68, (Feb. 1969).
6. Clear, A. J., Standard Laboratory Procedures for Determining Sensitivity, Brisance and Stability of Explosives, Technical Report No. 3278, Revision I, (April 1970).

Table 1

Reaction time as the variable in the reaction of nitrocellullose with phenyl isocyanate at 69°C, in tetrahydrofuran, for 5 hrs

Sample	Reaction Time Hr	Found % N		-ONC <sub>2</sub>	DS C <sub>6</sub> H <sub>5</sub> NHCO	DS Total
		-ONO <sub>2</sub>	Total			
A	1.5	10.66	11.87	2.22	0.27	2.49
B	6.0	9.84	11.77	2.17	0.43	2.60
C	18.0	9.86	11.89	2.21	0.45	2.66
D	42.0	9.19	11.53	2.10	0.54	2.64
E	66.0	9.03	11.53	2.13	0.58	2.71
F	120.0	8.61	11.32	2.05	0.63	2.68

Table 2

Reaction of nitrocellulose DS 2.44  
and DS 2.90 with phenyl isocyanate  
at 69°C, in tetrahydrofuran

Sample	Rea Time (Hr)	Type of NC (DS)	NC (Moles)	THF (ml)	DS of the Product		
					$\frac{-\text{ONO}_2}{2}$	$\frac{\text{RNHC=O}}{2}$	Total
A	5	2.44	0.010	20	2.29	0.29	2.58
B	66	2.44	0.010	20	2.13	0.58	2.71
C	5	2.90	0.010	20	No Reaction		
D	5	2.90	0.010	80	2.79	0.03	2.82



Table 3

Reaction of nitrocellulose with o-tolyl isocyanate in cyclohexanone, at 110°C

<u>Sample</u>	<u>Rea Time (Hr)</u>	<u>%N</u>		<u>DS</u>	
		<u>-ONO<sub>2</sub></u>	<u>Total</u>	<u>-ONO<sub>2</sub></u>	<u>RNH<sub>2</sub>=O</u>
88-1	1	10.88	11.62	2.17	0.15
88-2	3	9.74	10.87	1.95	0.23
88-3	5	8.74	10.25	1.86	0.36
88-4	7	8.21	10.39	1.80	0.48

Table 4

Reaction of nitrocellulose with m-tolyl  
isocyanate in cyclohexanone, at 110°C

Sample	Rea time (Hr)	%N		DS	
		-ONO <sub>2</sub>	Total	-ONO <sub>2</sub>	RNHC=O
88-5	1	9.28	11.00	2.00	0.37
88-6	3	8.75	10.76	1.92	0.44
88-7	5	8.21	10.47	1.82	0.50
88-8	7	8.06	10.56	1.85	0.57

Table 5

Reaction of nitrocellulose with p-tolyl  
isocyanate in cyclohexanone, at 110°C

<u>Sample</u>	<u>Rea Time (Hr)</u>	<u>%N</u>		<u>DS</u>	
		<u>-ONO<sub>2</sub></u>	<u>Total</u>	<u>-ONO<sub>2</sub></u>	<u>RNHC=O</u>
88-13	1	8.33	10.83	1.95	0.58
88-14	3	8.14	10.52	1.84	0.54
88-15	5	7.57	10.32	1.77	0.64
88-16	7	6.99	10.16	1.71	0.77

Table 6

Reaction of nitrocellulose with  
 tolyl isocyanate isomers

Rea Time (Hr)	DS of -ONO <sub>2</sub>			DS of RNHC=O		
	o-	m-	p-	o-	m-	p-
1	2.17	2.00	1.95	0.15	0.37	0.58
3	1.95	1.92	1.84	0.23	0.44	0.54
5	1.86	1.82	1.77	0.36	0.50	0.64
7	1.80	1.85	1.71	0.48	0.57	0.77

Table 7

Reaction of nitrocellulose with p-tolyl  
isocyanate at 69°C and at 110°C

Rea Time (Hr)	$\frac{-\text{ONO}_2}{69^\circ}$		$\frac{\text{RNHC=O}}{69^\circ}$		Total DS	
	69°	110°	69°	110°	69°	110°
1	2.29	1.95	.22	.58	2.51	2.53
3	2.26	1.84	.18	.54	2.44	2.38
5	2.12	1.77	.33	.64	2.45	2.41
7	1.96	1.71	.49	.77	2.45	2.48

Table 8

Effect of phenyl isocyanate upon cellulose nitrate  
phenyl carbamate 69°C, 5 hrs, in tetrahydrofuran

Sample	%N		DS		Yield	
	$\frac{-\text{ONO}}{2}$	Total	$\frac{-\text{ONO}}{2}$	$\frac{\text{C}_6\text{H}_5\text{NHC=O}}{1}$	gm	%
A	9.91	11.79	2.20	0.42	5.48	88.4
B	9.70	11.66	2.15	0.41	4.79	87.4
C	9.47	11.38	2.05	0.54	3.52	73.4
D	9.57	11.64	2.14	0.40	2.06	58.5

Table 9

Changes in DS of nitrocellulose and cellulose nitrate  
phenyl urethane under varied conditions

Operation or Reaction	Found % N		DS
	$\frac{-\text{ONO}_2}{2}$	Total	
A) Nitrocellulose (NC)	12.63		$\frac{2.44}{\text{C}_6\text{H}_5\text{NHCO}}$
B) Isolation & Purification of NC (No Heating)	12.49		2.42
C) Heating NC at 69°C for 48 hrs & Purification	12.37		2.38
D) NC Reacted With Phenyl Isocyanate at 69°C for 42 hrs	9.19	11.53	2.10
E) Product (D) Reacted Again As In (D)	8.48	11.05	1.93
			0.54
			0.58

Table 10

Effect of water upon the reaction of 0.01 mole of nitrocellulose with excess of phenyl isocyanate at 69°C, in tetrahydrofuran

Sample	Rea Time (Hr)	Quantity of water (ml)	%N		DS		DS Total
			-ONO <sub>2</sub>	Total	-ONO <sub>2</sub>	RNHC=O	
A	1	0.01	11.82	12.22	2.33	0.08	2.41
B	1	0.02	11.66	12.77	2.35	0.12	2.47
C	1	0.05	11.88	12.18	2.32	0.18	2.50
D	1	0.10	11.50	12.14	2.31	0.13	2.44
E	1	--	12.06	12.30	2.36	0.05	2.41
F	5	0.10	10.40	11.87	2.23	0.45	2.68
G	5	--	10.30	11.83	2.21	0.33	2.54



Table 11

Effect of dilution upon the reaction of 0.01 mole  
of nitrocellulose with excess of phenyl  
isocyanate at 69°C, in tetrahydrofuran, for 5 hr

Sample	THF (ml)	%N		DS		DS Total
		$\frac{-\text{ONO}_2}{2}$	Total	$\frac{-\text{ONO}_2}{2}$	$\frac{\text{RNHC=O}}{1}$	
1	20	10.71	12.06	2.29	0.29	2.58
2	40	10.21	11.74	2.18	0.33	2.51
3	80	10.68	11.76	2.19	0.22	2.41
4	60	10.87	12.08	2.29	0.04	2.33

Table 12

Effect of excess of phenyl isocyanate reacted with  
0.01 mole of nitrocellulose at 69°C, in tetrahydrofuran, for 5 hr

<u>Sample</u>	Phenyl Isocyanate (Moles)	%N		DS		<u>NS Total</u>
		<u>-ONO<sub>2</sub></u>	<u>Total</u>	<u>-ONO<sub>2</sub></u>	<u>RNHC=O</u>	
A	0.025	11.63	12.18	2.32	0.11	2.43
B	0.035	10.86	11.99	2.27	0.24	2.51
C	0.045	10.83	11.94	2.25	0.23	2.48
D	0.055	10.76	11.97	2.26	0.25	2.51
E	0.074	10.71	12.06	2.29	0.29	2.58

Table 13

Effect of stannous octoate catalyst upon the reaction of nitrocellulose with excess of phenyl isocyanate at 69°C, in tetrahydrofuran, for 5 hr

Sample	Reaction Time (Hr)	Found %N		DS		DS Total
		$\frac{-\text{ONO}_2}{2}$	Total	$\frac{-\text{ONO}_2}{2}$	$\frac{\text{C}_6\text{H}_5\text{NHCO}}{1}$	
A	1	10.83	12.01	2.27	0.25	2.52
B	2	10.74	12.00	2.27	0.27	2.54
C	5	9.64	11.71	2.17	0.47	2.64
D	43	9.10	11.32	2.03	0.57	2.60
E	66	9.84	11.32	2.03	0.56	2.59
F	120	8.10	10.82	1.84	0.62	2.46

Table 14

Effect of various catalysts upon the reaction of nitrocellulose with phenyl isocyanate at 69°C, in tetrahydrofuran, for 5 hr

<u>Sample</u>	<u>Catalyst</u>	DS		<u>DS Total</u>
		<u>-ONO<sub>2</sub></u>	<u>RNHCO</u>	
1	Tetrabutyltin	2.13	0.50	2.63
2	Butyltin Trichloride	2.17	0.48	2.65
3	Tributyltin Chloride	2.14	0.47	2.61
4	Stannous Octoate	2.17	0.47	2.64
5	Triethyl Amine	2.12	0.49	2.61
6	1,4-Diazabicyclo[2,2,2] Octane	2.11	0.41	2.52
7	None	2.29	0.29	3.58

Table 15

Effect of temperature upon the reaction of nitrocellulose  
with phenyl isocyanate in 1,4-dioxane, for 5 hr

<u>Sample</u>	<u>Rea Temp</u> (°C)	<u>Time</u> (Hr)	<u>%N</u>		<u>DS</u>		<u>DS</u> <u>Total</u>
			<u>-ONO<sub>2</sub></u>	<u>Total</u>	<u>-ONO<sub>2</sub></u>	<u>RNH<sub>2</sub>=O</u>	
A	70	5	11.44	12.05	2.28	0.12	2.40
B	77	5	11.31	12.02	2.27	0.14	2.41
C	100	5	9.39	11.55	2.11	0.49	2.60
D	100	30	8.11	10.75	1.82	0.59	2.41

Table 16

Stability of cellulose nitrate phenyl carbamate  
 DS 2.10-ONO<sub>2</sub> - 0.54 ØNCO and nitrocellulose 12.57%N

<u>Sample</u>	<u>SP</u> 134.5°C <u>(min)</u>	<u>RF</u> 134.5°C <u>(min)</u>	<u>Heating</u> at 134.5°C for 300 min	<u>Vac Stab</u> 100 C 40 hr <u>(MI)</u>	<u>Exp Temp</u> <u>(°C)</u>	<u>Imp Sens</u> 2 Kg/sq in
NC 12.57%N	30	40	No Expl	0.89	255	4
Cell Nitr Ph Carb	125	125	No Expl	0.81	Smoke 242-600	5

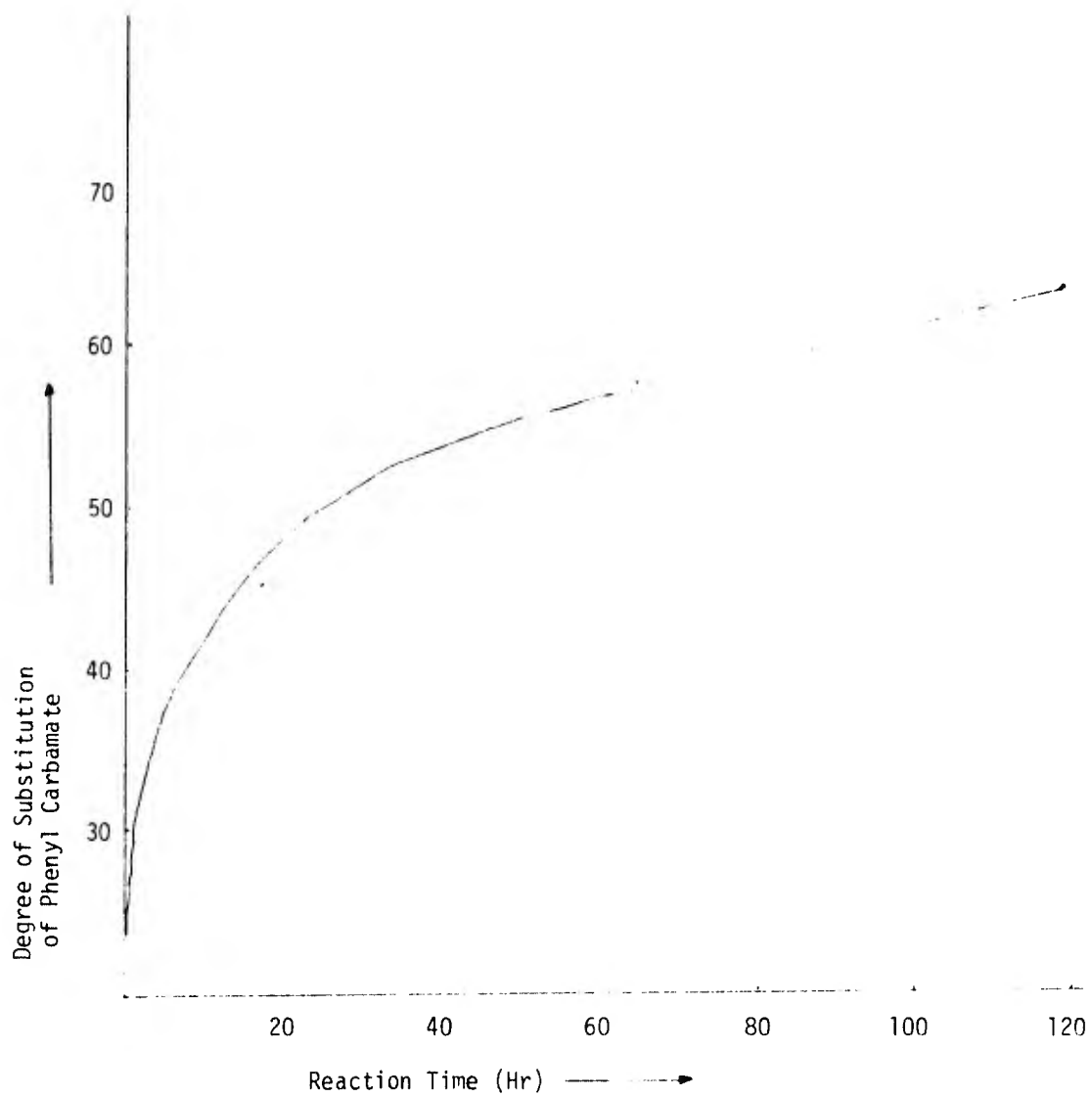


Fig 1 Degree of substitution of phenyl carbamate vs reaction time - no catalyst

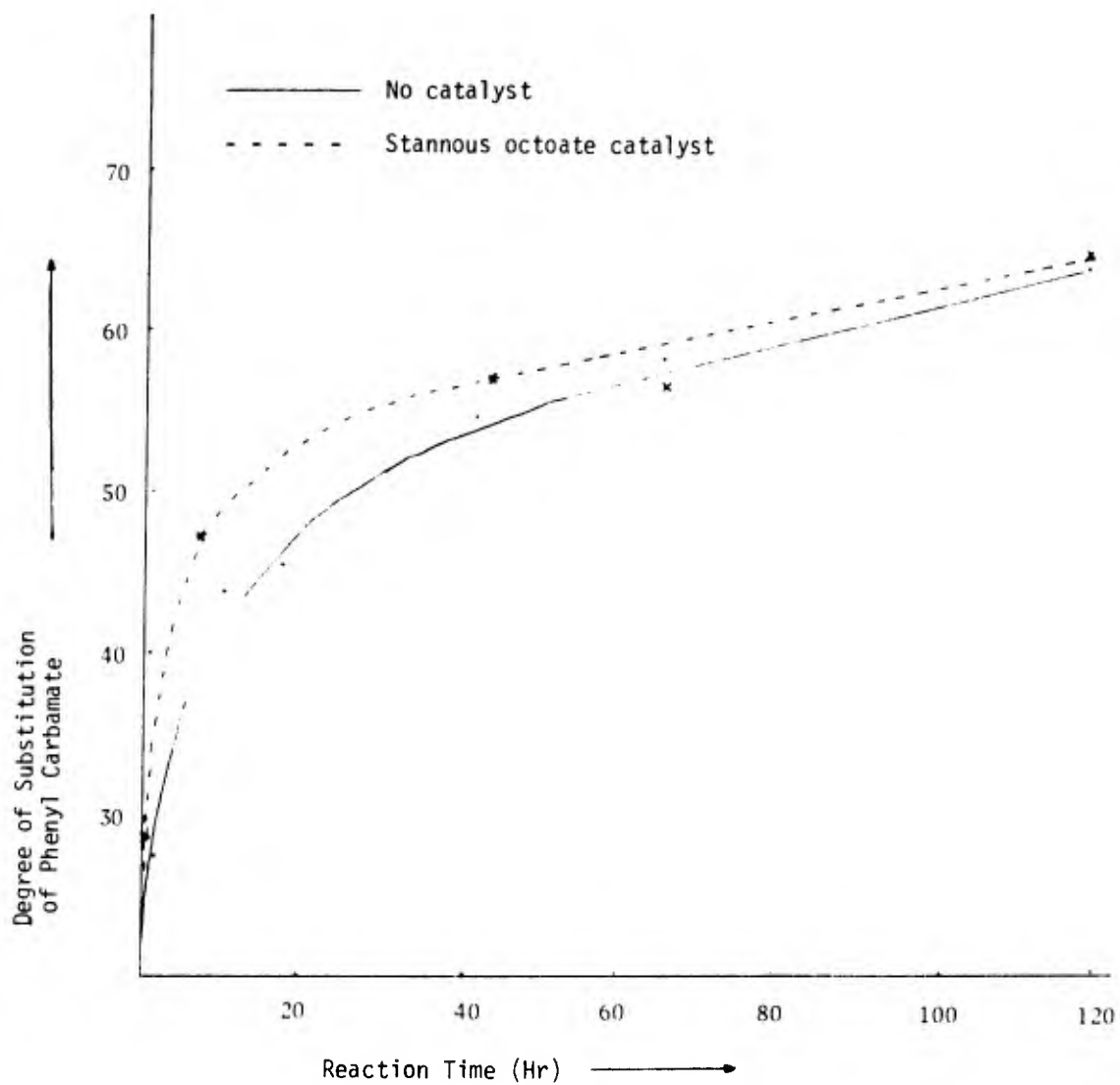


Fig 2 Degree of substitution of phenyl carbamate vs reaction time - stannous octoate catalyst