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SYNTHESIS AND EVALUATION OF CURING AGENTS

ANNUAL TECHNICAL REPORT
MARCH 4, 1968 - FEBRUARY 28, 1969

Prepared For

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards, California

By

A. H. Muenker, C. A. Rowe, M. Lynn,
P. E. Wei, J. Linsk and C. Gustavson
Esso Research and Engineering Company
Linden, New Jersey

Contract No. FO4611-68-C-0045

Esso Report No. GR-2-SEC-69
Esso Project 1150

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SYNTHESIS AND EVALUATION OF CURING AGENTS

By

A. H. Muenker, C. A. Rowe, M. Lynn, F. E. Wei,
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Annual Technical Report
March 4, 1969 - February 28, 1969

ESSO RESEARCH AND ENGINEERING COMPANY
GOVERNMENT RESEARCH LABORATORY
LINDEN, NEW JERSEY

FOREWORD

This report describes research studies aimed at the development of improved curing agents for binder prepolymers. The program consists of four phases which comprise a literature survey (Phase I), synthesis of new curing agents (Phase II), gumstock studies (Phase III) and small-scale propellant formulations (Phase IV). Phase IV and portions of Phase III are carried out by Lockheed Propulsion Company under subcontract. Results of the literature survey will be published as a separate report. Specific cure studies relating to Shell's P-BEP prepolymer will also be published in a separate interim report.

This is the first annual report of this investigation. The research is being carried out for the Air Force under Contract No. F04611-68-C-0045 and the program has been administered by Mr. Robert Corley, Captain Raymond Foscante and Dr. James Trout, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The work reported was done in the Government Research Laboratory of the Esso Research and Engineering Company, Linden, New Jersey and by Lockheed Propulsion Company, Redlands, California. Research was initiated March 4, 1968 and this report covers the period March 4, 1968 - February 28, 1969.

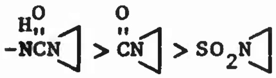
Research was carried out at Esso by Mr. A. H. Muenker (Project Leader) and Drs. C. A. Rowe, M. Lynn and P. E. Wei. Work at Lockheed Propulsion was carried out by Mr. C. Gustavson and Dr. J. Linsk. Other technical personnel were consulted on specific aspects of aziridine synthesis. The project is under the supervision of Dr. M. S. Cohen, Program Manager.

Publication of this report does not consitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

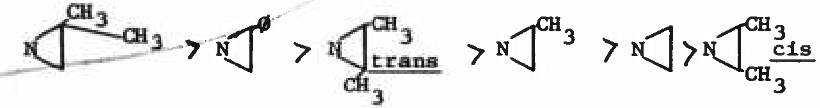
W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Curing agents for both carboxy and hydroxy-functional prepolymers have been investigated. A series of di- and trifunctional aziridines have been synthesized and evaluated. These include sulfonyl, acyl and ureido aziridines. Reactivity was found to decrease in the following order:



Reactivity and specificity of these aziridines is also affected by the substitution on the aziridine ring. The following order of decreasing reactivity was found:



The 2,3-dimethyl aziridines exhibit the highest degree of specificity. To get satisfactory cures with the sulfonyl aziridines a catalyst will be needed. Ureido and acyl 2,3-dimethyl aziridines give adequate cure rates at 150°F. ~~The~~ application of di/triisocyanate cure systems to hydroxy-terminated prepolymers has been limited in the past by the availability of commercial triisocyanates of acceptable purity. Two pure triisocyanates have been isolated from commercial sources and one of these has been evaluated in gumstocks. Mechanical properties of OH-Telagen-S gumstocks cured with di-/triisocyanates have shown that the maximum stress, initial modulus and Shore hardness is a function of diisocyanate structure and triisocyanate level whereas the maximum strain is solely dependent on the triisocyanate level. Aging studies of OH-Telagen-S gumstocks cured with di/triisocyanate have shown that the urethane cure linkage has adequate thermal stability at 275°F.

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I. INTRODUCTION

To arrive at a criterion of curative selection, those forces acting on the curative during the cure cycle and subsequently on the cure linkage in the acidic propellant environment must be well understood and taken into consideration. Curatives are highly reactive chemical compounds which are designed to perform a specific task. They must selectively and under certain restricted time-temperature regimes react with functional groups on the polymer chain without reacting with other highly reactive chemicals which are present in the same medium. They must, furthermore, cease reacting after the programmed period of cure has ended and must establish strong, thermally and hydrolytically stable linkages.

Curatives in use today are plagued with a host of side reactions all of which produce undesirable mechanical characteristics in the end-item propellant. Notably among these undesirable reactions are:

(1) self-destruction reactions such as homopolymerization or rearrangements.

(2) post cure phenomena which increase the hardness of the propellant

(3) reversion of cure by chemical or thermal processes and

(4) acid-base reactions or compound formation of the curative or cure linkage with the oxidizer.

Ideal curatives should meet the following criteria:

1. The curative functional group reaction will not produce any small molecules.

2. The curative in its unreactive form will not be basic.

3. The curative will not generate basic sites after reacting with the functional groups of the prepolymer.

4. The curative will not be capable of easy self-polymerization.

5. The curative will not be capable of reacting with the oxidant.

6. The curative will have a high temperature coefficient of reactivity (it will be essentially unreactive towards functional groups at room temperature but will react readily at cure temperatures).

7. The curative-functional group reaction product will not undergo easy hydrolytic cleavage.

8. The curative will either be a liquid or should be readily dispersible in the propellant binder.

In practice a compromise between these desirable properties may be necessary.

Various phenomena must be considered and isolated in the evaluation of new curing agents if the data are to guide the synthesis efforts towards the achievement of optimum structures. An analysis of the mechanical properties, and of changes in mechanical properties as a function of sample history (temperature-humidity-time) provides a gross overall evaluation. Such an evaluation must be conducted using both gumstock and propellant to define the physical and the chemical consequence of adding filler materials.

The area of synthetic activity which possesses the greatest possibility of short term success is that which is built around derivatives of known curative type functionalities such as aziridines, epoxides and isocyanates by selecting the most suitable structural and electronic modifications of these curative types.

To provide criteria for improvement over state-of-the-art cure systems, two "baseline" systems will be used as controls. The Telagen CT/HX-868 and Butarez CT/HX-868 will serve as base cases for carboxy-terminated prepolymers cured with the presently used trifunctional aziridine, HX-868.

TDI in combination with a triol will be used as the baseline cure system for the OH-Telagen prepolymer. In addition, it is desirable to utilize data obtained from at least one well characterized propellant as a basis for interpretation of propellant properties obtained with new curatives.

This report describes the initial results of studies relating the effect of type and number of substituents on the aziridine ring to reactivity and specificity with carboxylic acid functional groups. Di- and trifunctional derivatives of the most interesting aziridine structures have been synthesized. Initial evaluation of these curatives in Butarez gumstocks is discussed.

With respect to isocyanate cure systems for OH-terminated binders we have initially taken the position that there is presently no convincing evidence for the need of new isocyanate structures. However, it was felt that two factors required further studies: One factor was the lack of commercially available triisocyanates of acceptable purity. Methods to isolate pure triisocyanates from commercial sources were therefore explored. The second factor arises from the fact that there is a relatively large number of different diisocyanate structures available. The question arises therefore whether there is a preferred diisocyanate structure which will give optimum mechanical properties.

II. OBJECTIVE

The objective of this program is to develop a series of curing agents exhibiting optimum stability in the presence of other propellant ingredients, producing the most thermally and chemically stable cure linkage and yielding mechanical properties better than state-of-the-art systems. Curing agents for both carboxy- and hydroxy-functional prepolymers will be investigated. The curing agents to be developed are expected to be generally applicable to all prepolymers of the same functional end groups (OH or COOH).

In order to concentrate on the influences of curative structure upon stability and minimize effects of prepolymer structure, it was deemed important to use prepolymers (saturated and unsaturated) having essentially the same backbone chain structure. For this reason the following Telagen prepolymers were chosen:

(1) COOH-Telagen nominal Mn: 4500

(2) COOH-Telagen-S nominal Mn: 2000

(3) OH-Telagen nominal Mn: 4500

(4) OH-Telagen-S nominal Mn: 2000

The Telagen prepolymers are functionally-terminated polybutadienes prepared by General Tire and Rubber Company. The letter S denotes the saturated (hydrogenated) analogue. Because of the higher viscosity of the saturated prepolymers a lower molecular weight prepolymer is dictated.

Since the Telagen prepolymer series was not immediately available for gumstock studies, the COOH-Butarez, type II (nominal molecular weight 4500) was initially used for the evaluation of new curing agents in gumstocks.

Part of this program also involved cure studies with the P-BEP binder and the selection of an optimum cure system for this binder. P-BEP is an energetic binder produced by Shell Development Company. The results of these studies will appear in a separate interim report.

Cure systems were also to be developed for the functionally terminated polyperfluoroalkylene oxide developed by 3M. It now appears that this prepolymer will not become available for this program.

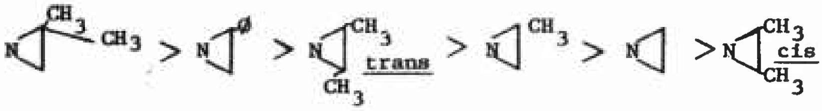
III. SUMMARY

This report discusses research aimed at the development of improved curing agents for binder prepolymers. This is the first annual report and covers the period March 4, 1968 through February 28, 1969.

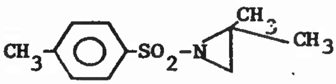
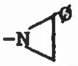
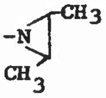
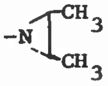
Sulfonyl aziridines are being investigated as potential curatives for carboxy-terminated polymers. It was considered that a cure between a sulfonyl aziridine and a carboxy group would give a unique grouping with resistance to post-curing and hydrolytic degradation. In addition the sulfonyl aziridines are stable compounds which form mildly acidic adducts after reaction with carboxy acids, and they cannot rearrange to oxazolines.

As a first step in determining the suitability of sulfonyl aziridines as potential curing agents for carboxy-terminated polymers a series of monofunctional model arylsulfonyl aziridines were prepared and reacted with model carboxylic acids. The aziridine structures were varied both in the organosulfonyl and the aziridine moiety to cover as large a range in reactivity as possible.

Rate studies of the sulfonyl aziridines were carried out in excess acetic acid at 50°C. The results obtained by following the disappearance of aziridine, show that the reactivity of sulfonyl aziridines is affected by substitution on the aziridine as follows:



The reactivities of these sulfonyl aziridine structures with excess acid at 50°C are illustrated by the following half-lives:

	t1/2		t1/2
	2 min		30 hrs
	22 min		34 hrs
	2 hrs		43 hrs
Trans		Cis	

The rate of the aziridine-carboxylic acid reaction is therefore a function of (1) the number of substituents, (2) the type of substituents and (3) the position of the substituents on the aziridine ring. Although substitution on the aziridine ring had a major effect on reactivity and selectivity, substituents on the phenyl ring of the N-aryl sulfonyl aziridines had only secondary effects on reactivity.

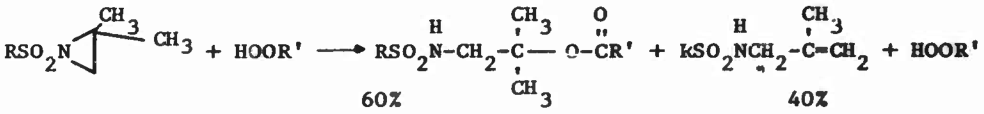
Reactivity of these aziridines with carboxylic acids is of course only one consideration. Selectivity, that is the extent to which the desired sulfonamide ester linkage is formed, is of even greater concern. Analysis of the reaction products of the various aziridines with carboxylic acids showed that the 2,3-dimethyl aziridine had the highest selectivity and was therefore the preferred structure.

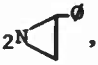
Reaction of the 2,3-dimethyl aziridine with carboyxlic acids gave the corresponding sulfonamide-ester in essentially quantitative yield:

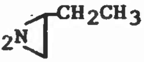
essentially quantitative

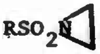
Below we have summarized the reasons for rejecting the other aziridine structures:

The 2,2-dimethyl aziridines, although exhibiting the highest rate, had the lowest selectivity, forming consistently about 40% of the corresponding olefin by elimination of the acid:

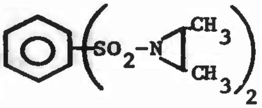


The 2-phenyl aziridine, RSO₂N , was rejected because it would considerably increase the equivalent weight of the curative.

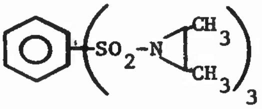
The monoethyl derivative, RSO₂N , was found to consistently homopolymerize.

The monomethyl, RSO₂N , and nonsubstituted aziridines, RSO₂N , exhibited fair to good selectivity but offered no improvement in reactivity over the 2,3-dimethyl aziridines. In fact, the trans-2,3-dimethyl aziridine had greater reactivity than the mono- and nonsubstituted aziridines.

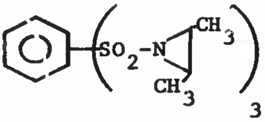
Based on the model compound studies, one difunctional and two trifunctional sulfonyl aziridine curatives were prepared and evaluated with Butarez CTL Type II prepolymer. The three curatives that were prepared and evaluated were the cis-2,3-dimethyl aziridine of m-benzene disulfonylchloride (I) and the cis- (II) and trans-2,3-dimethyl aziridine (III) derivatives of S-benzene trisulfonylchloride.



(I) cis



(II) cis



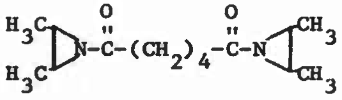
(III) trans

The slow rate of cure of the sulfonyl aziridines at a stoichiometric aziridine/COOH ratio and in a dilute system which approximates the binder cure situation became apparent quite early in the cure studies. Satisfactory cures could not be obtained at 150°F. At 180°F only the trans-2,3-dimethyl sulfonyl aziridines gave a satisfactory cure. At 200°F the trans-2,3-dimethyl derivative cured within 1 day, and the cis-2,3-dimethyl system cured in 2 days.

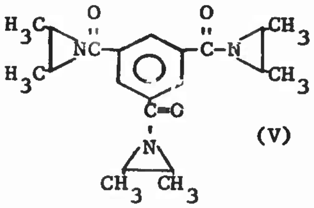
To get satisfactory cure rates with the sulfonyl aziridine system for propellant applications catalyst will be needed. Catalyst studies are being conducted with $BF_3\cdot$ complexes. Although catalytic activity of these complexes is generally quite high, there was evidence that selectivity was adversely affected, presumably due to catalyzed homopolymerization of the aziridines.

Since the sulfonyl aziridines exhibited low reactivity we are investigating the 2,3-dimethyl acyl aziridines as an approach to increase the cure rate over that of the sulfonyl aziridines, while retaining the selectivity of the 2,3-dimethyl aziridine structure. The 2,3-dimethyl acyl aziridines have much better storage stability than HX-868 (the 2-ethyl aziridine of trimesic acid), which undergoes oxazoline rearrangement during room temperature storage and is therefore shipped under dry ice conditions. The 2,3-dimethyl acyl aziridines also have better selectivity than HX-868 and they exhibit a faster cure rate than the sulfonyl aziridines but a lower cure rate than HX-868.

One difunctional aliphatic (IV), and one trifunctional aromatic cis-2,3-dimethyl aziridine (V) were synthesized by reacting the corresponding acyl chlorides with cis-2,3-dimethyl aziridine.



(IV)



(V)

The reactivity of HX-868 and the cis-2,3-dimethyl aziridine analogue (V) with octanoic acid in toluene was determined at 150°F. Under these conditions HX-868 has a half-life of 58 hours, whereas the cis-2,3-dimethyl analogue has a half-life of 8 days. There is apparently a 3 to 4 fold difference in reactivity between the monoethyl (HX 868) and the cis-2,3-dimethyl aziridine (compound V).

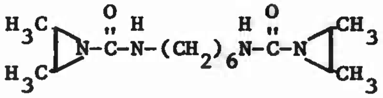
Preliminary evaluations of the above cis-2,3-dimethyl aziridines were carried out with Butarez Type II CTPB. Gumstocks were prepared at varying tri-/difunctional curative ratios and cured at 150°F.

As expected the maximum strain was strictly a function of the trifunctional aziridine content decreasing with increase in triaziridine content. The maximum stress increased rapidly with triaziridine content and leveled off at a 50/50 di-/trifunctional ratio. The initial modulus showed essentially a linear increase with increase in trifunctional curative.

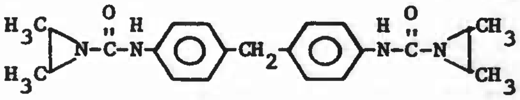
At the 50/50 di-/trifunctional curative level using the cis-2,3-dimethyl acyl aziridines both the maximum stress and strain levels are considerably greater than Butarez gumstocks cured with HX-868. Propellant demonstration is necessary to determine whether there is a significant difference in mechanical properties resulting from the use of cis-2,3-dimethyl aziridine curatives as compared to HX-868.

In conclusion, it can be stated that the cis-2,3-dimethyl acyl aziridines are stable curatives which require no special storage conditions. They exhibit greater cure rates than sulfonyl aziridines but lower reactivity than monosubstituted acyl aziridines (HX-868). They also have better selectivity than monosubstituted acyl aziridines.

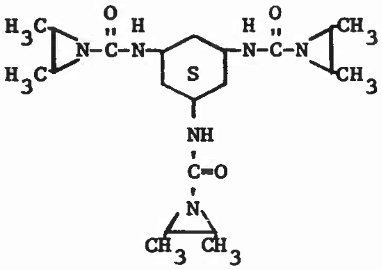
The third aziridine system that is being investigated is based on ureido aziridines. This system was selected because it provided another approach to further increase the rate of cure. Replacing the N-substituent with a less electron withdrawing group should increase its reactivity. The cis-2,3-dimethyl aziridine was chosen again because of its proven high selectivity when reacting with carboxylic acids. The following five di- and trifunctional derivatives were synthesized from the corresponding isocyanates in yields exceeding 90%:



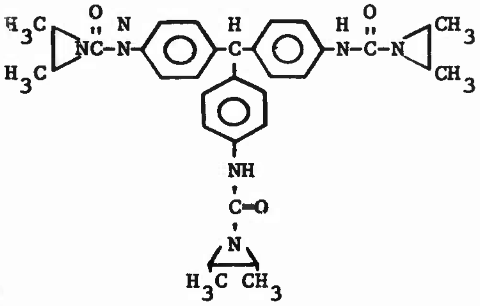
(VI)



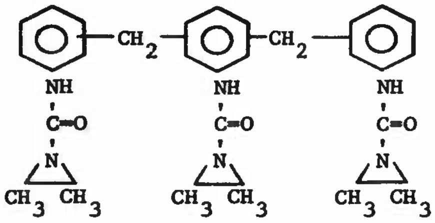
(VII)



(VIII)



(IX)



(X)

The ureido aziridines are all white, very fluffy solids which can be readily dispersed in the prepolymer.

The reactivity of ureido aziridines with carboxylic acids is considerably greater than that of the corresponding acyl aziridines. For instance the half-life with octanoic acid in toluene at 150°F is 4 hours as compared to 8 days for the corresponding acyl aziridines.

Gumstock studies with Butarez CTPB have been made using combinations of tri- and difunctional aromatic and aliphatic ureido aziridines. Gumstocks were cured for 4 days at 150°F.

As anticipated the strain values increased with decreasing trifunctional aziridine level, and maximum stress and initial modulus decreased with decreasing trifunctional curative level. The maximum strain values follow the same dependence for both the aliphatic and aromatic difunctional aziridines except for a slight divergence at very high levels of difunctional curative. This same independence of maximum strain on the structure of the difunctional curative has been observed for the isocyanate cured OH-Telagen-S system.

At every di-/trifunctional level the aromatic difunctional curative resulted in a higher maximum stress level than the aliphatic difunctional curative.

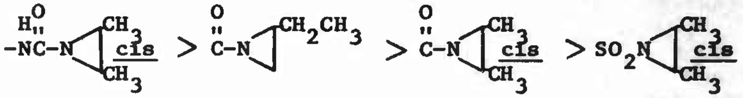
The initial modulus showed an essentially linear increase with increase in trifunctional level, the aromatic difunctional curative resulting in a higher modulus than the aliphatic difunctional ureido aziridine.

Thermal aging studies were carried out with the Butarez-aziridinyl ureido gumstocks at 275°F in a nitrogen atmosphere.

At low levels of trifunctional curative there is a significant decline in both maximum stress and strain as a result of heat aging at 275°F in a nitrogen atmosphere. At the higher levels of trifunctional curative there is very little degradation in properties and the gumstocks appear to retain their properties much better than the HX-868 cured gumstock.

To summarize our findings with respect to cis-2,3-dimethyl aziridinyl ureido curatives we found that they are stable compounds which can be stored at room temperature. They are fluffy solids which are readily dispersed in the propellant binder. They are more reactive than acyl or sulfonyl aziridines and have good selectivity with carboxylic acids. Ureido aziridines are readily synthesized in high yields from the corresponding isocyanates. Because of their high reactivity, they may require lower processing temperatues to give adequate propellant pot-life.

In summary, the reactivity of the three aziridine systems with carboxylic acids was found to decrease in the following order:



The lack of available triisocyanates of acceptable purity prompted studies to purify commercially available products. Two products which were of particular interest are PAPI and MONDUR M. PAPI is Upjohn's tradename for polymethylene polyphenylisocyanate. This material is a dark-colored nonvolatile liquid, which according to the manufacture is approximately a trifunctional polyisocyanate. Mobay Chemical Company markets triphenyl methane triisocyanate under the tradename, MONDUR TM. It is a brown to brownish purple liquid which is sold as a 20% solution in methylene chloride. Both of these triisocyanates are quite impure which has limited their application as crosslinking agents for OH-terminated propellant binders.

Our analyses of PAPI have shown that it has the following approximate composition:

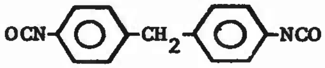
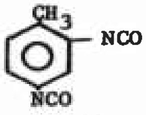
- 49% Diisocyanate
- 22% Triisocyanate
- 29% Residue (Polyfunctional)

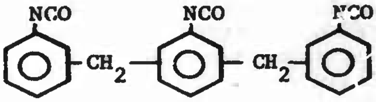
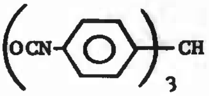
A two-step technique was developed to isolate the pure triphenyl dimethylene triisocyanate. The method involves (1) separation of the undesirable, highly colored components by precipitation and (2) subsequent vacuum distillation of the filtrate to isolate pure di- and triisocyanate. The pure triphenyl dimethylene triisocyanate is a white to light yellow solid of M.P. about 70°C and is isolated in about 10-15% yield.

Pure triphenyl methane triisocyanate was similarly isolated from MONDUR TM. The distilled triisocyanate is an off-white solid which is isolated in about 50% yield. NMR data show that all isocyanates on the triphenyl methane triisocyanates are para-substituted.

Rate studies have been carried out with OH-Telagen-S (secondary OH) at ambient temperature using four different diisocyanates and two triisocyanates. The reaction profiles were determined by infrared measurements by following the disappearance of the isocyanate band at 4.4μ using the 3.4μ band as an internal reference. As expected, the three aromatic di- and triisocyanates showed considerably greater reactivity than the aliphatic diisocyanate.

The 50% conversion points for four different diisocyanates and two triisocyanates with OH-Telagen-S at ambient temperature are summarized below:

Isocyanate	Structure	t (1/2) (50% Conversion) (Hours)
Diphenyl methane diisocyanate		1
2,4-Tolylene diisocyanate		6
Bitolylene diisocyanate		9
Hexamethylene diisocyanate	$OCN(CH_2)_6NCO$	30

Isocyanate	Structure	t (1/2) (50% Conversion) (Hours)
Triphenyl dimethylene triisocyanate		1
Triphenyl methane triisocyanate		<30 minutes

The effect of CH_3-groups ortho to the NCO group on reactivity is clearly demonstrated in the case of bitolylene diisocyanate. The methyl substituent ortho to the isocyanate groups reduced the reactivity about ten-fold. 2,4-Tolylene diisocyanate shows an intermediate effect, having only one isocyanate group blocked by a methyl group. This substitution effect on reactivity provides a convenient key to control the reactivity of aromatic isocyanates.

The hexamethylene diisocyanate chain extender exhibiting a half-life of about 30 hours showed considerably lower reactivity than the aromatic diisocyanates. This is also reflected by practical experience which shows that aliphatic diisocyanates provide longer pot-life than aromatic diisocyanates.

One of the main objectives in the evaluation of isocyanates was to determine the effect of diisocyanate structure and di-/triisocyanate ratio on such mechanical properties as maximum stress, strain at maximum stress, initial modulus and hardness of gumstocks. Since there is a relatively large number of different diisocyanate structures available, the question arises whether there is a preferred diisocyanate structure which will give optimum mechanical properties.

Mechanical property measurements were made on cured OH-Telagen-S gumstocks using micro-dumbbells at a crosshead speed of 2 inches/minute. Gumstocks were prepared at a 1/1 stoichiometric NCO/OH ratio and cured at 150°F for 6 days. The following variables were investigated:

- Di-/triisocyanate ratio from 9/1 to 100% triisocyanate.
- Four different diisocyanate structures.
- Temperature, ambient and 180°F
- The effect of aging at 275°F for 7 days in a nitrogen atmosphere.

On the basis of mechanical property measurements on OH-Telagen-S gumstocks we offer the following conclusions.

As expected, the % strain at maximum stress (also equal to maximum strain) sharply decreases with increase in triisocyanate level reaching a minimum at the 100% triisocyanate level. The decrease in strain level is most severe at triisocyanate equivalent levels from 0-50%. Most significantly, differences in the structure of diisocyanates have only secondary effects on the maximum strain level. From the standpoint of optimizing the maximum strain level there is apparently no preferred diisocyanate structure. The strain level is solely dependent on the triisocyanate level. At 180°F the strain at maximum stress is significantly reduced for each comparable di-/triisocyanate ratio, resulting in a lower but similar curve as compared to the ambient temperature dependence of maximum strain on triisocyanate level. Differences in the structures of the diisocyanates have again no significant effect on the maximum strain level.

The maximum stress (also equal to the stress at break) at ambient temperature shows a dual dependence on (a) triisocyanate level and (b) structure of the diisocyanate.

For both hexamethylene diisocyanate and tolylene diisocyanate chain-extended gumstocks, the maximum stress level increases with increase in triisocyanate level. Tolylene diisocyanate reaches the maximum stress level at about 40 equivalent % of triisocyanate whereas the aliphatic diisocyanate, HDI, requires a triisocyanate level in excess of 60% to reach maximum stress.

Gumstocks which are chain extended with diphenyl methane diisocyanate show an independence of maximum stress level with triisocyanate concentration.

Bitolylene diisocyanate shows a very unique behavior. The maximum stress decreases with increase in triisocyanate level, reaching a plateau at the 40-60% triisocyanate level. The fact that maximum stress increased with increase in diisocyanate content must reflect the structural behavior of this particular diisocyanate. Bitolylene diisocyanate contains the very rigid biphenyl linkage which apparently dictates the maximum stress level.

At 180°F, there is a significant reduction in stress level as compared to ambient temperature at every comparable triisocyanate level.

Aromatic diisocyanates very definitely result in higher maximum stress levels than the aliphatic diisocyanate at comparable triisocyanate levels. Most significantly there is no difference in stress level between the three aromatic diisocyanate structures. This is in contrast to measurements at ambient temperature where there is a definite effect of aromatic diisocyanate structure on stress level. The observed strong dependence of diisocyanate structure on maximum stress at ambient temperature must therefore be due to secondary effects: differences in the degree of entanglement, association between cure linkages or hydrogen bonding. At the elevated temperature (180°F) the secondary effects are negated.

The initial modulus at ambient temperature shows an almost linear increase with increase in triisocyanate level for three of the four diisocyanates (HDI, TDI, DPMD). The bitolylene diisocyanate again occupies a unique position showing a maximum-initial modulus at the high diisocyanate content. This high initial modulus is very undesirable for propellant applications.

At 180°F the initial modulus shows a very steep increase with increase in triisocyanate level. Although the aliphatic diisocyanate results in the lowest initial modulus at comparable triisocyanate levels the spread between the four diisocyanate structures is not very pronounced. The effect of diisocyanate structure on initial modulus has been greatly reduced at the elevated temperature (180°F).

The Shore "A" hardness also shows an essentially linear increase with increase in triisocyanate level for HDI, TDI and DPMD. Bitolylene diisocyanate again shows a maximum at the high diisocyanate level reaching a minimum at 20 to 40 equivalent % triisocyanate. Both the initial modulus and the Shore "A" hardness show the same directional dependence on triisocyanate level for the four diisocyanates.

OH-Telagen-S gumstocks cured with the same di-/triisocyanates previously discussed were heat aged at 275°F in a nitrogen atmosphere for 7 days. The resulting mechanical properties at ambient temperature reveal no significant changes upon thermal aging at 275°F. These data show that urethane binders will have adequate thermal stability at the 275°F temperature level over the stated test period. Based on these data also there is no preferred diisocyanate structure from the standpoint of heat aging properties at 275°F. All cure systems have shown excellent thermal aging behavior on the OH-Telagen-S gumstock.

In conclusion it can be stated that:

Maximum strain at a given temperature is solely dependent on triisocyanate level - independent of diisocyanate structure.

Maximum stress, initial modulus and Shore "A" hardness at ambient temperature are a function of diisocyanate structure and triisocyanate level.

At ambient temperature as well as 180°F the use of aromatic diisocyanates results in higher maximum stress levels than aliphatic diisocyanates at comparable triisocyanate levels.

Aromatic diisocyanates require lower triisocyanate level than aliphatic diisocyanates to attain a given stress level and hence permit higher maximum strain capability.

At 180°F differences in the structure of aromatic diisocyanates have no effect on the maximum stress level.

Urethane binders have adequate thermal stability at 275°F (7 days).

IV. TECHNICAL PROGRESS

A. SYNTHESIS AND EVALUATION OF SULFONYL AZIRIDINES

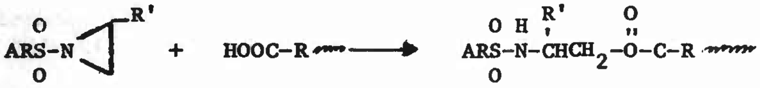
Sulfonyl aziridines are being investigated as potential curatives for carboxy-terminated prepolymers. It was considered that a cure between a sulfonyl aziridine and a carboxy group would lead to a unique grouping with resistance to post-curing and hydrolytic degradation. As a first step in determining the suitability of sulfonyl aziridines as potential curing agents for COOH-terminated prepolymers, we have synthesized a series of monofunctional model sulfonyl aziridines. The aziridine structures were varied both in the organosulfonyl and the aziridine moiety to cover as large a range in reactivity as possible. Synthesis and evaluation of these compounds is discussed in the following sections.

1. Synthesis of Monofunctional Model Curatives Based on Sulfonyl Aziridines

The use of arylsulfonyl aziridines as potential curing agents for carboxy-terminated prepolymers has not been studied as extensively as acyl aziridines and aziridinyl phosphine oxides. Acyl aziridines are known to undergo rearrangement during the cure cycle to form the oxazoline ring. This self-destruction reaction depletes the number of functional groups which can react with the prepolymer. As a result, propellants cured with this class of aziridines exhibits poor mechanical properties. The reaction products of aziridinyl phosphine oxides with the COOH-functional groups of the prepolymer are subject to hydrolytic cleavage with resultant loss of propellant strength.

The sulfonyl aziridines, however, are stable compounds which form mildly acidic adducts after reaction with the COOH-function, and most significantly, they cannot rearrange to oxazolines.

As a first step in determining the suitability of sulfonyl aziridines as potential curing agents for COOH-terminated prepolymers, we have synthesized a series of monofunctional model arylsulfonyl aziridines. The reaction of these aziridines with carboxylic acids would result in a sulfonamide-ester linkage as illustrated below.



Carboxy-terminated prepolymers cured with di- and trifunctional analogues of these aziridines are expected to exhibit better hydrolytic and high temperature thermal stability than those cured with either acyl aziridines or aziridinyl phosphine oxides.

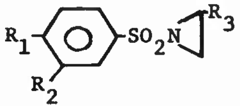
A total of 18 model arylsulfonyl aziridines have been synthesized to date. Their structures and properties are listed under each subheading in this section. Infrared spectra of representative model aziridines are found in the appendix. All are white solids at room temperature with the exception of N-[p-toluene sulfonyl]-2-ethyl aziridine which melts at about

24°C. All compounds were purified by recrystallization from carbon tetrachloride-pentane mixtures until no change in the infrared spectra or melting points was observed.

1.1. N-[Arylsulfonyl]-Mono and Nonsubstituted Aziridines

Two derivatives were made from a nonsubstituted aziridine, four from a 2-methyl aziridine, one from a 2-ethyl aziridine, and two from 2-phenyl aziridine. Elemental analyses and observed melting points are listed in Table I.

TABLE I



					Analysis(a) Found (Cal'cd)			
R_1	R_2	R_3	m.p. (°C)	Yield,%	C	H	N	S
H	H	H	45-45°	--	52.88 (52.44)	5.23 (4.95)	8.42 (7.64)	--
H	H	CH_3	57-58.5°	78				
CH_3	H	H	64-64.5	29	54.73 (54.78)	5.88 (5.62)	7.13 (7.14)	
CH_3	H	CH_3	63.5-64.2°	60	56.90 (58.85)	6.32 (6.20)	7.01 (6.63)	
CH_3	H	C_2H_5	24-25°	--	59.65 (58.64)	6.50 (6.71)	6.81 (6.22)	--
CH_3	H	C_6H_5	90-91°	61	65.51 (65.92)	5.90 (5.53)	4.95 (5.13)	
H	NO_2	CH_3	49-51°	--	44.46 (44.62)	4.35 (4.76)	11.71 (11.56)	
CH_3O	H	CH_3	48°	67	52.48 (52.85)	5.79 (5.77)	6.01 (6.16)	
H	H	C_6H_5	70-70.5°	68	64.84 (64.84)	5.14 (5.06)	5.05 (5.40)	

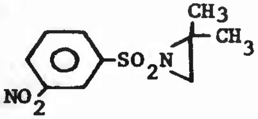
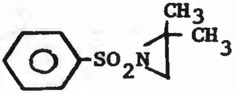
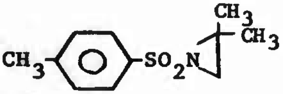
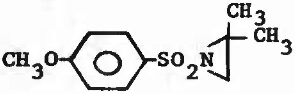
(a) All agreed with Cal'cd. within 0.4% unless otherwise stated.

All of the aziridines in this group with one exception are solid and stable at room temperature. N-[p-tolylsulfonyl]-2-ethyl aziridine was a low melting white solid 24-25°C. On several occasions this material polymerized readily at ambient conditions.

1.2. N-[Arylsulfonyl]-2,2-Disubstituted Aziridines

A total of four 2,2-dimethyl substituted aziridines were prepared to determine the effect of 2,2-disubstitution on (1) reactivity with octanoic acid and (2) selectivity towards addition reaction with octanoic acid. The four compounds are listed below (Table II).

TABLE II

	m.p. (°C)	Yield, %$^{(a)}$	C	N
	105-106	75	47.07 (46.97)	10.80 (10.93)
	83-84	54	--	--
	97.5-98.5	74	58.62 (58.67)	6.15 (6.22)
	58.5-59	59	53.86 (54.75)	5.61 5.83

(a) After recrystallization from carbon tetrachloride:pentane

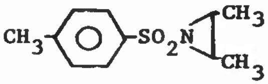
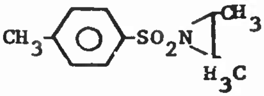
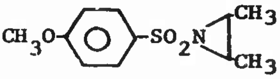
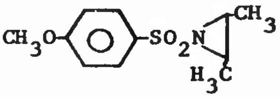
Several of these compounds were not stable at room temperature and had to be stored at 0°C.

1.3. N-[Aryl Sulfonyl]-2,3-Disubstituted Aziridines

During the course of our studies on the reactivity of mono- and 2,2-disubstituted aziridines we had observed that 2,2-disubstituted aziridines were more reactive than mono-substituted aziridines. We, therefore, extended our synthesis effort to 2,3-disubstituted aziridines to determine the effect of 2,3-disubstitution on reactivity and selectivity.

A total of four 2,3-disubstituted aziridines were made. Two of these were prepared from cis-2,3-dimethyl aziridine and two from trans-2,3-dimethyl aziridine. Their structures are listed below:

TABLE III

		m.p.°C	Yield %(a)	Anal. C	H	N
	cis	93-94	76	58.88 (58.64)	6.79 (6.71)	6.32 (6.22)
	trans	76-77	60	58.52 (58.64)	6.51 (6.71)	6.28 (6.22)
	cis	72.72.5	40	52.88 (54.75)	6.32 (6.27)	5.08 (5.83)
	trans	71-71.5	81	54.67 (54.75)	6.26 (6.27)	5.80 (5.83)

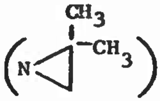
(a) Recrystallized yield, from carbon tetrachloride:pentane.

1.4. N-[Alkyl Sulfonyl]-Aziridines

Two butane sulfonyl derivatives of 2-methyl and 2,2-dimethyl aziridines were prepared to compare the reactivity with that of N-[aryl sulfonyl] aziridines. Again the selectivity of these sulfonyl aziridines towards addition reaction was of equal concern. The specific structures are shown below.

TABLE IV

N-ALKYL SULFONYL AZIRIDINES

n-$C_4H_9SO_2$-R		b.p., °C	n_D^{20}	Yield
R				
2-Methylaziridine		65-67 (0.1 mm)	1.4607	55
2,2-Dimethylaziridine		85-86 (0.17mm)	--	73

2. Reaction of Sulfonyl Aziridines With Model Carboxylic Acids

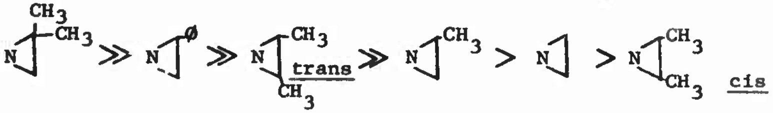
Kinetic studies have been carried out to determine the reactivity and selectivity of monofunctional sulfonyl aziridines with carboxylic acids. Octanoic acid was chosen as a suitable replica of COOH-terminated prepolymers. Acetic acid was used in some of the studies because it was easier to isolate and purify the acetate ester than the octanoate ester.

Several factors are of primary interest in determining the suitability of a given aziridine structure as a potential curing agent for COOH-terminated prepolymers:

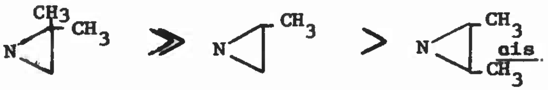
- Stability of the neat compound at room temperature
- Reactivity with carboxylic acids (octanoic acid serves as our model acid)
- Relative tendency for addition reaction vs. homopolymerization or other side reactions in the presence of the carboxylic acids.
- Stability and compatability of the cure linkage with oxidizers.

Of all the monofunctional aziridines studied to date only one, N-[p-toluene sulfonyl]-ethyl aziridine, exhibits a tendency to homopolymerize when stored neat at room temperature. All other sulfonyl aziridines are stable at room temperature.

Rate studies of sulfonyl aziridines were carried out in excess acetic acid at 50°C. The reactions were followed by titration for remaining aziridine. The results show that the reaction of aziridine with excess acetic acid is pseudo first order and that reactivity of sulfonyl aziridines is affected by substitution on the aziridine ring as follows:



Rate studies of sulfonyl aziridines with octanoic acid were carried out neat as well as in solution at stoichiometric aziridine/acid ratios. Solution kinetics were studied at 150°F or below. This temperature level reflects the upper temperature limit of conventional propellant cure conditions. Reactions were monitored by IR following the reduction of the azirdine ring deformation band and the appearance of the NH band. The disappearance of the octanoic acid and formation of the ester were also followed qualitatively by IR. In addition the acid was monitored quantitatively by base titration. The results of these studies show that the reactivity of sulfonyl aziridines is affected by substitution on the aziridine ring as follows:



This agrees with kinetic studies carried out with excess acetic acid.

2,2-Dimethyl sulfonyl aziridines have consistently exhibited higher reactivities than either the 2,3-dimethyl or monosubstituted aziridines. This higher reactivity has also been confirmed by a trifunctional-2,2-dimethyl aziridine which showed rates comparable to that of the monofunctional analogue. Analysis of the reaction products of the 2,2-dimethyl aziridines with octanoic acid, however, showed consistently a high percentage of unreacted acid, indicating that a side reaction was occurring. Reaction products from three different 2,2-dimethylaziridines with carboxylic acid show the presence of unsaturated sulfonamide as a substantial by-product. The formation of the unsaturated sulfonamide explains the presence of residual acid after all of the aziridine has reacted. Because of the formation of the unsaturated sulfonamides from 2,2-dimethyl sulfonyl aziridines, work with 2,2-dimethyl aziridines was terminated.

2,3-Dimethyl sulfonyl aziridines, although less reactive than the 2,2-dimethyl aziridines, yield only small amounts of unreacted octanoic acid indicating that the desired addition reaction has selectively taken place. Analysis of the end product also shows only one compound which is consistent with the anticipated sulfonamide ester.

Although substitution on the aziridine ring has a major effect on reactivity and selectivity, substituents on the phenyl ring of the N-aryl sulfonyl aziridines had only secondary effects on reactivity. Also N-alkyl sulfonyl aziridines were found to be somewhat less reactive than the N-aryl sulfonyl aziridines.

Details of the kinetic studies are described in the following sections. Studies are in progress to catalyze the reaction of sulfonyl aziridines with acids without adversely affecting selectivity towards the addition reaction.

2.1. Mono- and Nonsubstituted Sulfonyl Aziridines

In general, the mono- and non-substituted sulfonyl aziridines have exhibited low reactivities with carboxylic acids. Type and position of substituents on the benzene ring of the N-aryl sulfonyl aziridines have only secondary effects on reactivity. Analysis of the end product from the reaction of monosubstituted aziridine with carboxylic acids (octanoic and acetic acid) showed the presence of only one compound which is consistent with the anticipated sulfonamide ester.

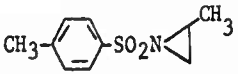
a. N-aryl Sulfonyl Aziridines

Out of nine mono- and nonsubstituted sulfonyl aziridines studied to date, only one, N-[p-toluene sulfonyl]-ethyl aziridine, exhibits a tendency to homopolymerize when stored neat at room temperature. All the other sulfonyl aziridines are stable at room temperature.

Octanoic Acid Studies

We have studied the kinetics of the reaction of a series of mono- and nonsubstituted sulfonyl aziridines with octanoic acid, a model carboxylic acid, at stoichiometric ratios of the reactants. The reactions were monitored by infrared absorption measurements using benzene ring absorption at 6.32μ or the sulfonyl absorption band at 7.58μ as internal references and selecting a suitable aziridine peak for analysis (11.8μ).

Non- and monosubstituted sulfonyl aziridines react slowly with octanoic acid, neat at 150°F. Reaction times in excess of 7 days are required at this condition for essentially complete reaction of the aziridine. Figures 1 and 2 show the rate of disappearance of aziridines for a mono- and nonsubstituted sulfonyl aziridine at 150°F. Comparison of Figures 1 and 2 shows that the reactivity of the monosubstituted aziridine is similar to that of the nonsubstituted aziridine. Zirconium acetyl acetonate at the 5% level has a moderate effect on reactivity (see Figure 2). Since initially our main concern was to determine whether the reaction of sulfonyl aziridine with octanoic acid would selectively and stoichiometrically form the sulfonamide ester, we speeded up the reaction by increasing the reaction temperature to a level (250°F) at which the reaction rate was sufficiently great so that the addition product could be formed in a reasonable time. Figure 3 shows the reaction profile of N-[p-methoxyphenyl sulfonyl]-2 methyl aziridine with octanoic acid, neat at 250°F. Repeated infrared spectra taken during the reaction at 250°F showed no evidence of thermal instability. All spectral changes during the reaction (disappearance of aziridine and acid bands and formation of ester bands) were consistent with the desired reaction product.

Fig. 1 Reaction of neat  with octanoic acid (1/1) at 150°F.

Rate of disappearance of aziridine as monitored by infrared absorption measurements

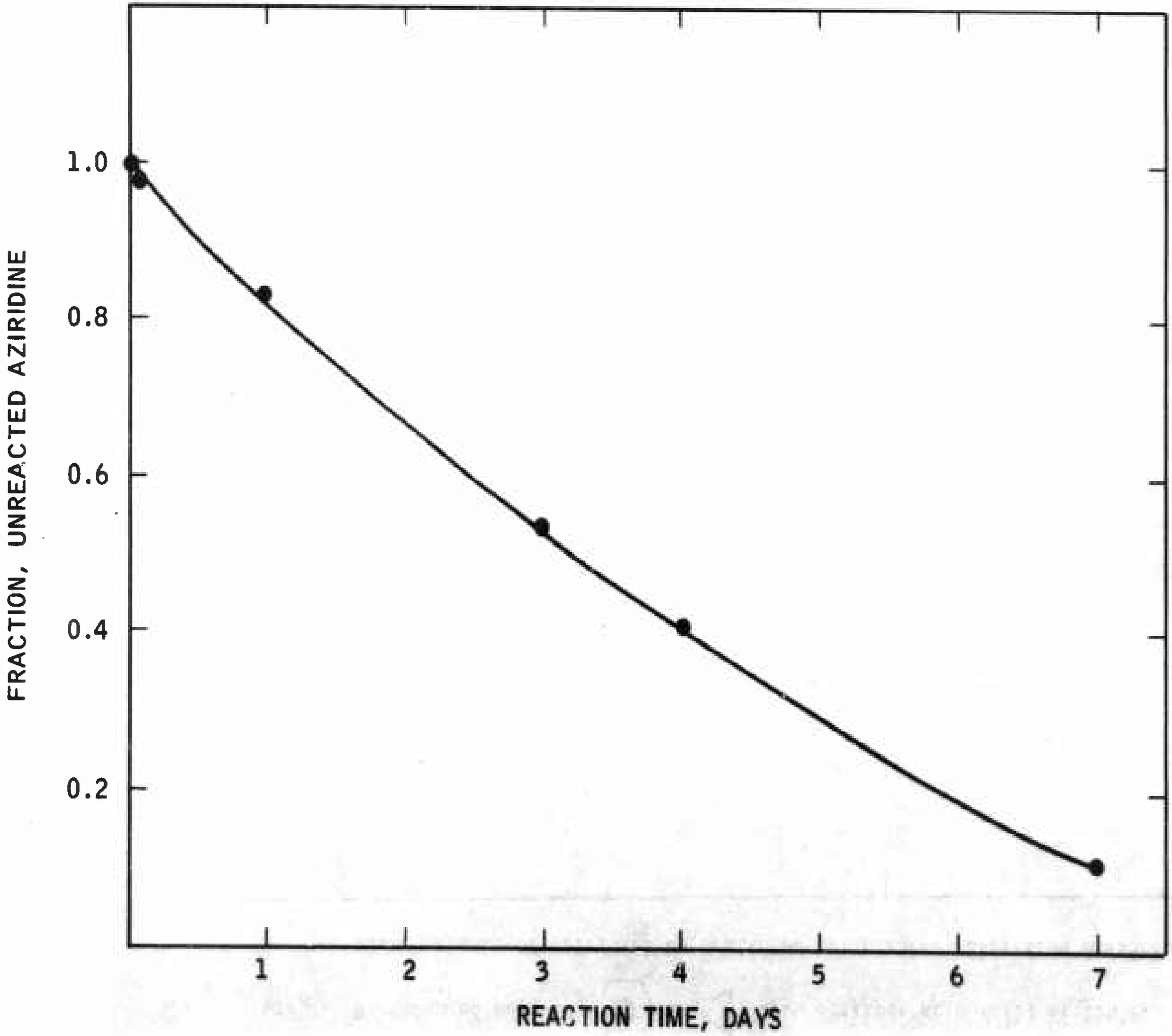
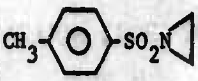


Fig. 2. Reaction of neat  with octanoic acid (1/1) at 150°F. Rate of disappearance of aziridine as monitored by infrared absorption measurements.

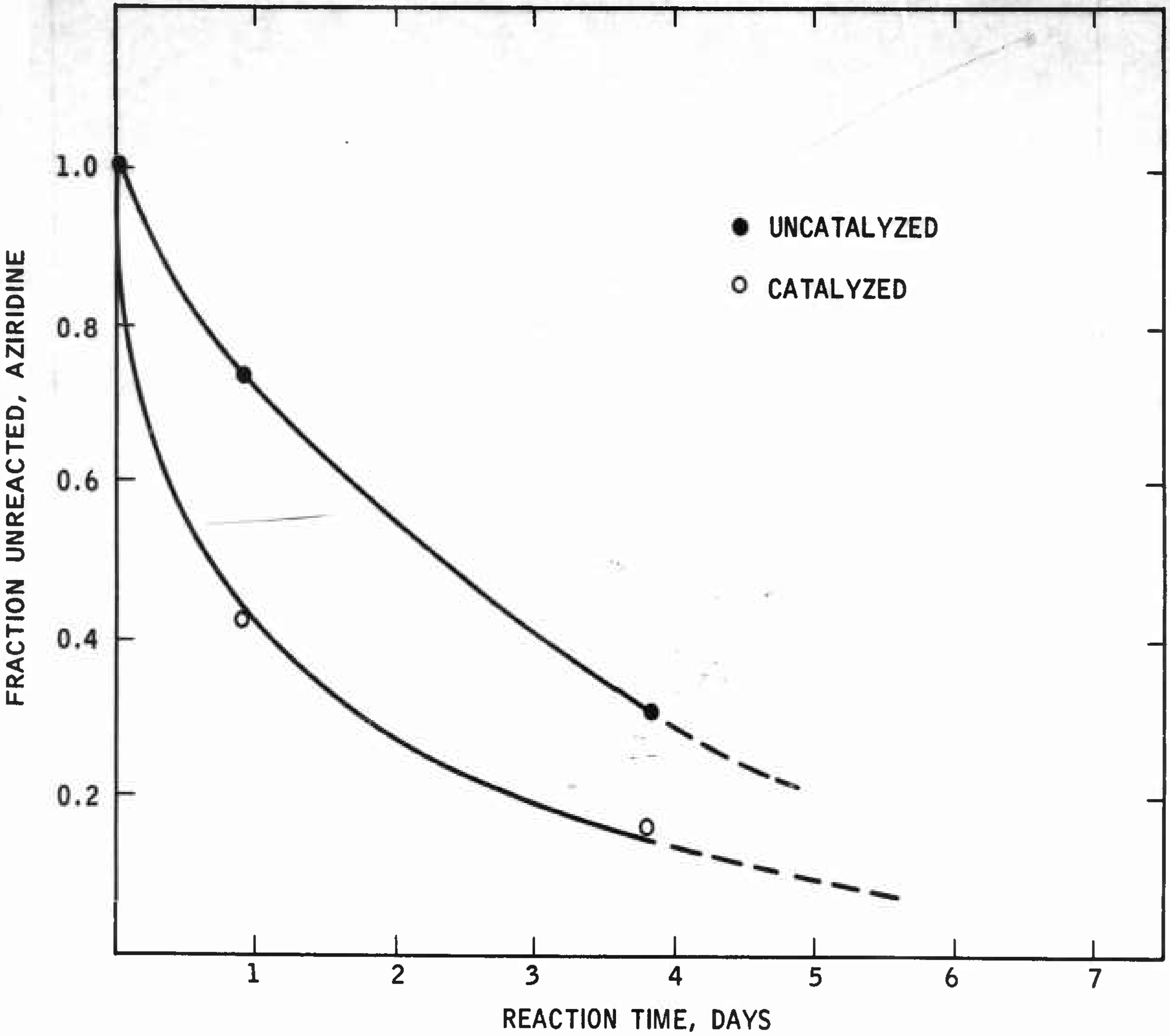
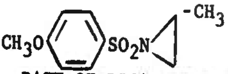
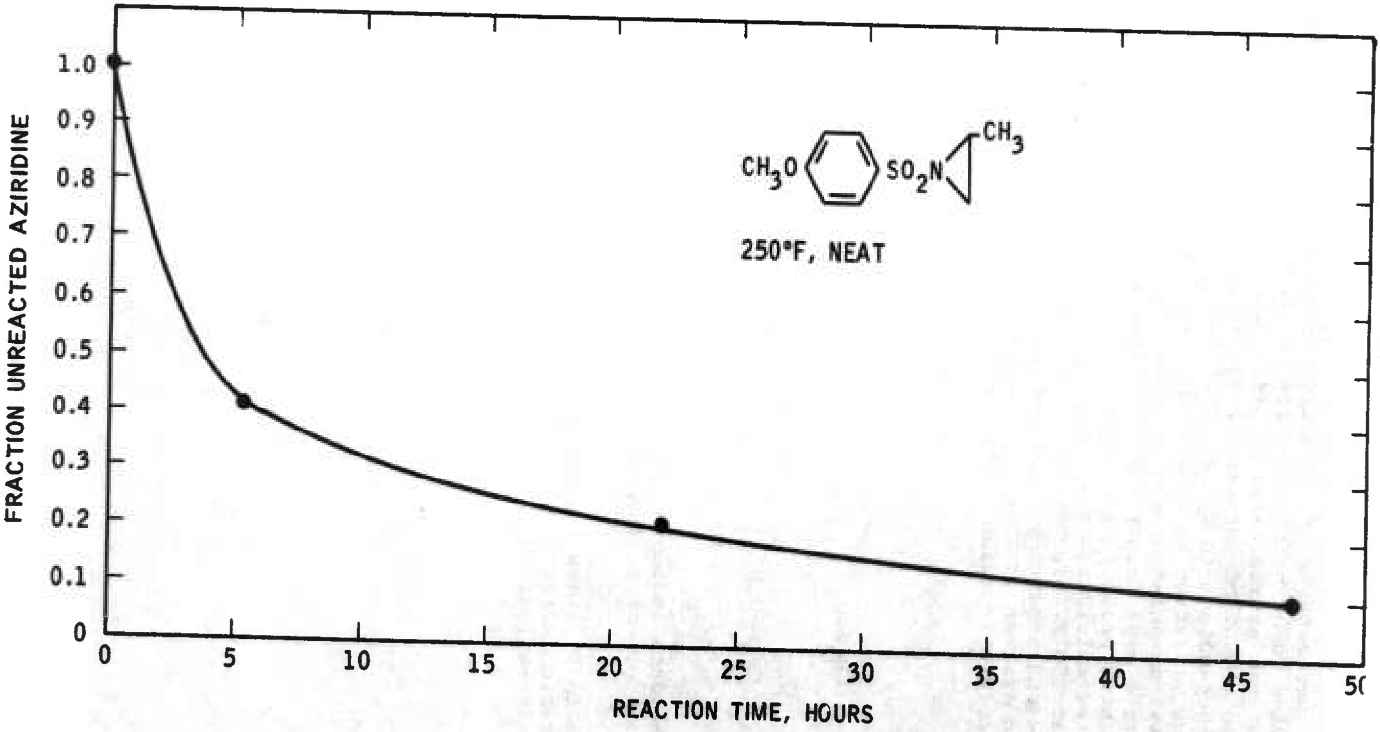
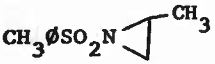
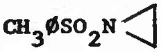


FIGURE 3

REACTION OF NEAT  WITH OCTANOIC ACID (1/1) AT 250°F. RATE OF DISAPPEARANCE OF AZIRIDINE AS MONITORED BY INFRARED ABSORPTION MEASUREMENTS



The percentages of unreacted octanoic acid after complete conversion of the aziridine is of particular concern since it greatly reflects upon the suitability of the aziridine as an effective curing agent. We therefore determined the amount of unreacted octanoic acid by base titration for a series of aziridine-octanoic acid systems. At the end of the reaction when the aziridine ring vibration band had completely disappeared, the product was titrated with tetrabutyl ammonium hydroxide to determine the amount of unreacted octanoic acid. (Separate experiments had shown that neither the unreacted aziridine nor the authentic product (sulfonamides) interferes with the titration.) Since monosubstituted aziridines react relatively slowly at 150°F, the reaction was carried out at 250°F. To determine that the high temperature level had no effect on the end product we compared the results for two model aziridine-octanoic acid systems at both 150°F and 250°F. Again titration was carried out after complete reaction of the aziridine. The data are summarized below.

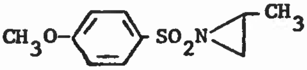
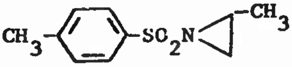
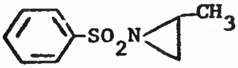
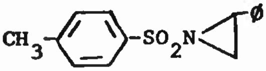
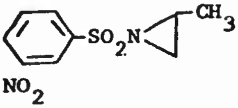
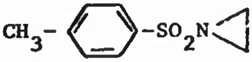
	% Unreacted Octanoic Acid	
	150°F	250°F
	5.1, 5.9	7.0
	29.3	27.8

The data indicate quite clearly that the temperature level has no significant effect on the end product.

Table V lists the percentages of residual octanoic acid found by base titration after complete reaction of the aziridine at 250°F. Numbers in parenthesis reflect the % unreacted acid after reaction at 150°F.

TABLE V

OCTANOIC ACID RECOVERY AFTER REACTIONS WITH AZIRIDINES (1:1) AT 250°F (TITRATION METHOD)

Aziridine Structure	Reaction Time (Hours)	Acid Recovery (%)
	65	3.4
	17 (> 7 days)	7.0 (5.1,5.9)
	17	10.6
	17	14.1
	65	16.3
	17 (> 7 days)	27.8 (29.3)

The percentage unreacted octanoic acid in the case of monosubstituted aziridines varied from as low as 3% to 16%, indicating that addition reaction is primarily taking place. A high percentage of unreacted octanoic acid would indicate a tendency of the aziridine to undergo side reactions, notably homopolymerization. Analyses of the reaction product from monomethyl sulfonyl aziridines and carboxylic acids discussed in Section 3.3 showed only one compound which is consistent with the anticipated sulfonamide ester.

The nonsubstituted aziridine showed a significantly higher level of unreacted acid (28-29%) suggesting a tendency towards homopolymerization.

For purposes of comparison we studied also the reaction of octanoic acid with two representative nonsulfonyl containing aziridines: (1) dodecyl aziridine ($C_{12}H_{27}N\lhd$) and (2) bis-aziridinyl propane ($\rhd N-CH_2-CH_2CH_2N\lhd$). These compounds readily and selectively undergo homopolymerization at room temperature in the presence of octanoic acid. By comparison this clearly points out the modifying effect of the sulfonyl group on the tendency of the aziridine ring to undergo homopolymerization.

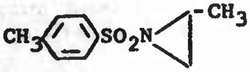
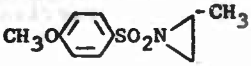
One of the program objectives of this contract is to develop suitable curatives for 3M's carboxy-terminated prepolymer, containing the very reactive perfluorocarboxylic group. We therefore studied the reaction of N-benzenesulfonyl-2-methylaziridine with trifluoroacetic acid, a model acid presumable reflecting the reactivity of the carboxy groups of the 3M prepolymer. The reaction was carried out neat at room temperature. Immediate reaction took place upon addition of trifluoroacetic acid as evidenced by heat generation. The infrared spectrum of the reaction product showed complete disappearance of the aziridine ring deformation band at 11.8 μ and an intense NH stretching peak at 3.08 μ giving definite indication that the desired addition reaction took place. This aziridine structure is apparently too reactive to be considered for 3M's perfluoroalkyleneoxide polymer.

To consider this type of aziridine structure as a potential curative for propellants, the cure rate must be significantly improved. Subsequent studies on mono-substituted sulfonyl aziridines were therefore directed towards improving the reactivity of these aziridines through catalysis. All studies were carried out in solution (o-dichlorobenzene) to simulate the dilution effect of the polymer chain on reactivity.

Zirconium acetyl acetonate ($Zr(AcAc)_4$) had previously been shown to have a moderate effect on the reaction of sulfonyl aziridines with octanoic acid when reacted neat. We therefore carried out reaction rate studies of monosubstituted sulfonyl aziridines in 20% solution (o-dichlorobenzene) at 150°F in the presence of 5% Zr $(AcAc)_4$. The monomethyl substituted aziridines showed very low reactivity even in the presence of the zirconium catalyst. In the table below are summarized the percentages of unreacted aziridine after 6 days at 150°F.

TABLE VI

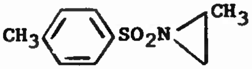
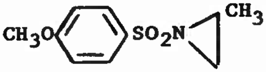
REACTION OF SULFONYL AZIRIDINES WITH OCTANOIC ACID IN 20% SOLUTION (o-DICHLOROBENZENE) AT 150°F, IN THE PRESENCE OF 5% $Zr(AcAc)_4$

Aziridine	% Aziridine Unreacted After 6 Days
	83 88*
	88

* without catalyst

Since Zr(AcAc) has only moderate catalytic activity, other catalysts were explored. BF_3 etherate has very high catalytic activity. Even at the low level of 0.2 wt. % BF_3 etherate, reactivity is too high at room temperature. Figures 4 and 5 show the reaction profiles of N-[p-methoxyphenyl sulfonyl]-2-methyl aziridine and N-[p-toluene sulfonyl]-2-methyl aziridine with octanoic acid in 20% solution at room temperature. Within one hour 80-90% of the aziridines reacted.

Titration of the reaction product with base after complete reaction of the aziridine, however, showed the presence of substantial amounts of unreacted acid.

	% Unreacted Octanoic Acid After Complete Reaction of Aziridine
	31.0
	43.3

It is quite evident from these data that the BF_3 catalyst not only catalyzes the addition reaction with octanoic acid but also promotes homopolymerization. The extent of homopolymerization is shown in Table VII where the disappearance of the aziridine was followed by IR. No octanoic acid was present in this study.

TABLE VII

REACTION OF N-(p-TOLUENEOSULFONYL-2-METHYL AZIRIDINE WITH $BF_3 \cdot OEt_2$

(16.2% aziridine concentration in o-dichlorobenzene with 0.89% $BF_3 \cdot OEt_2$)

Reaction Time	% Aziridine Remaining (1)
5 min.	100
40 min.	87.3
3.2 hours	80.0
6 hours	32.0
23.5 hours	18.6

(1) Determined by IR

It is quite evident that the extent of homopolymerization in the presence of the BF_3·etherate is considerable with the monomethyl aziridine derivative.

FIGURE 4

REACTION OF  WITH OCTANOIC ACID (1/1) IN 20% SOLUTION (O-DICHLOROBENZENE) AT ROOM TEMPERATURE IN THE PRESENCE OF 0.2% BF_3·ETHERATE

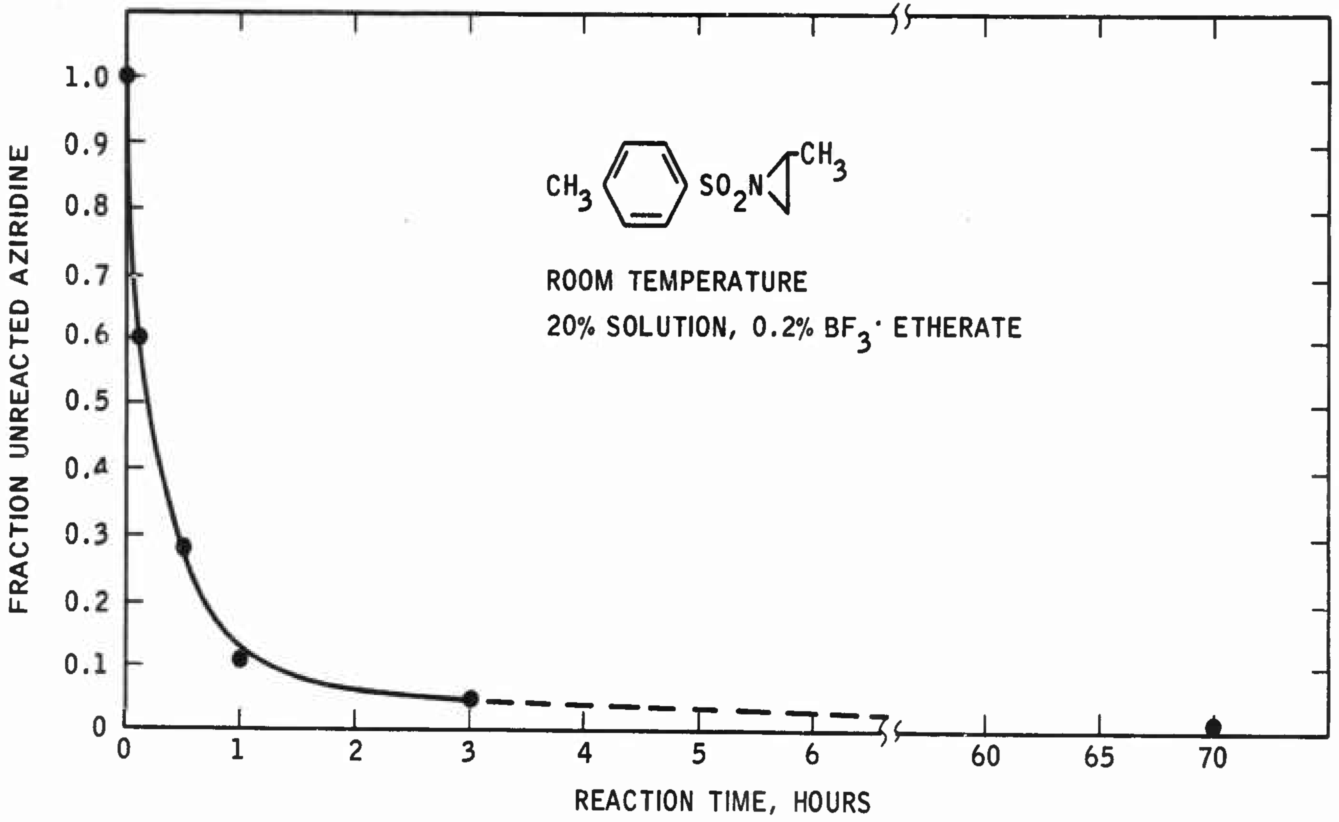
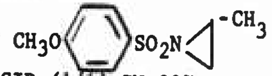
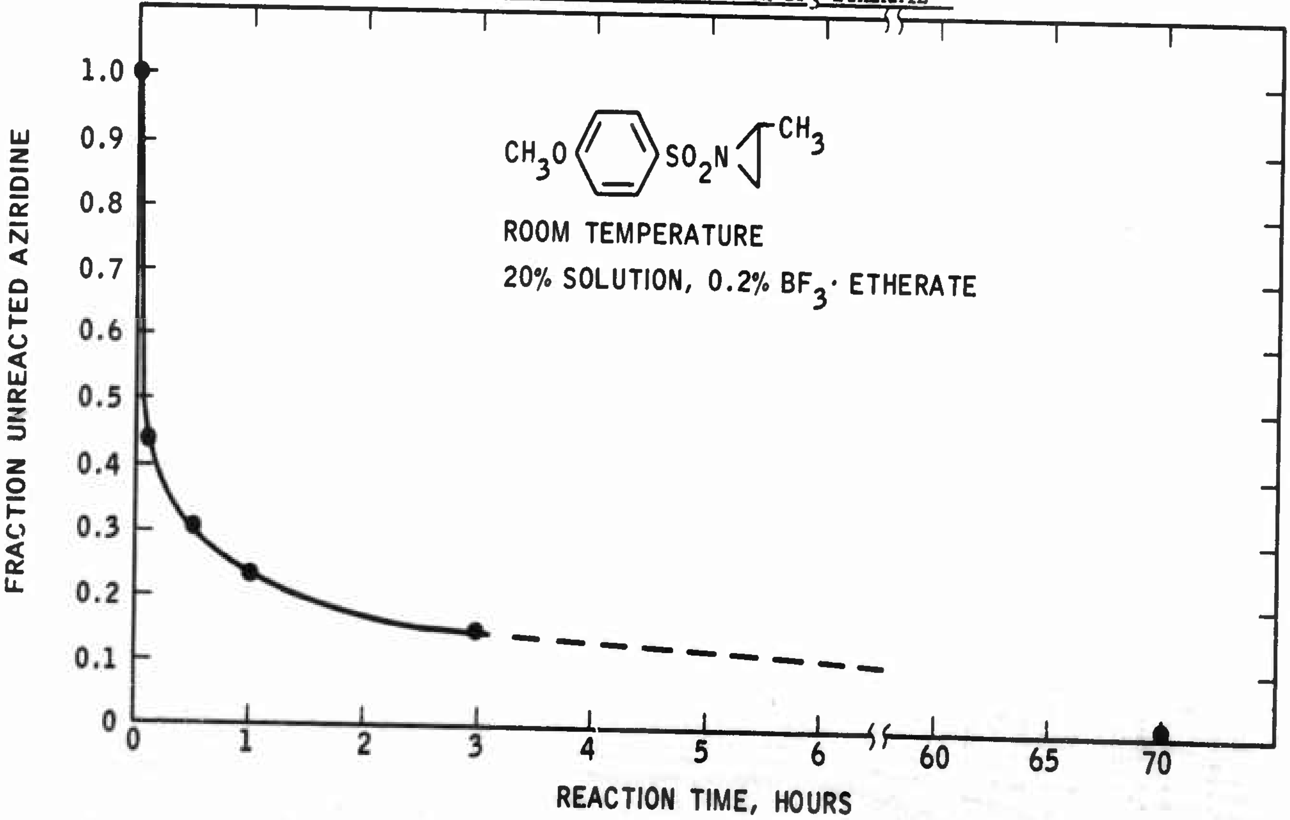


FIGURE 5

REACTION OF 

WITH OCTANOIC ACID (1/1) IN 20% SOLUTION (o-DICHLOROBENZENE) AT ROOM TEMPERATURE IN THE PRESENCE OF 0.2% BF_3·ETHERATE



Acetic Acid Studies

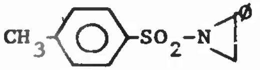
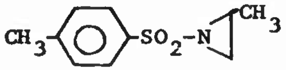
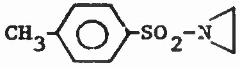
Rate studies were carried out with one nonsubstituted and two monosubstituted sulfonyl aziridines in excess acetic acid at 50°C (122°F). The reactions were followed by titrating the remaining aziridine with perchloric acid in the presence of tetrabutyl ammonium iodide. The results show that the reaction of aziridines in excess acid is pseudo-first order, and that the 2-phenyl derivative reacts considerably faster than the 2-methyl and non-substituted derivatives.

Figure 6 shows the rate of disappearance of aziridine for the reaction of N-[p-toluenesulfonyl]-2-phenyl aziridine with excess acetic acid at 50°C. Figure 7 shows the rate of disappearance of aziridine for the reactions of N-[p-toluenesulfonyl]-aziridine and N-[p-toluenesulfonyl]-2-methyl aziridine with excess acetic acid at 50°C.

A comparison of the half-lives of the three reactions is given below.

TABLE VIII

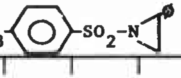
REACTION OF SULFONYL AZIRIDINES WITH EXCESS ACETIC ACID AT 50°C

Aziridine	$t_{1/2}$
	22 1/2 minutes
	29 1/2 hours
	34 hours

The 2-phenyl derivative reacts considerably faster than the 2-methyl and non-substituted derivatives. It is a little surprising that there is only a small difference in rate between the 2-methyl and non-substituted derivatives.

However, even the 2-phenyl substituted sulfonyl aziridine is relatively slow compared to the 2-ethyl aziridine of trimesic acid (HX-868). In the reaction of excess acetic acid with aziridine at room temperature HX-868 has a half-life of slightly over 2 minutes while the 2-phenyl sulfonyl aziridine has a half-life of slightly over 6 hours. It is quite clear that a catalyst is needed in order to make the sulfonyl aziridines useful as curatives.

FIGURE 6

REACTION OF CH_3  WITH ACETIC ACID AT 50°C

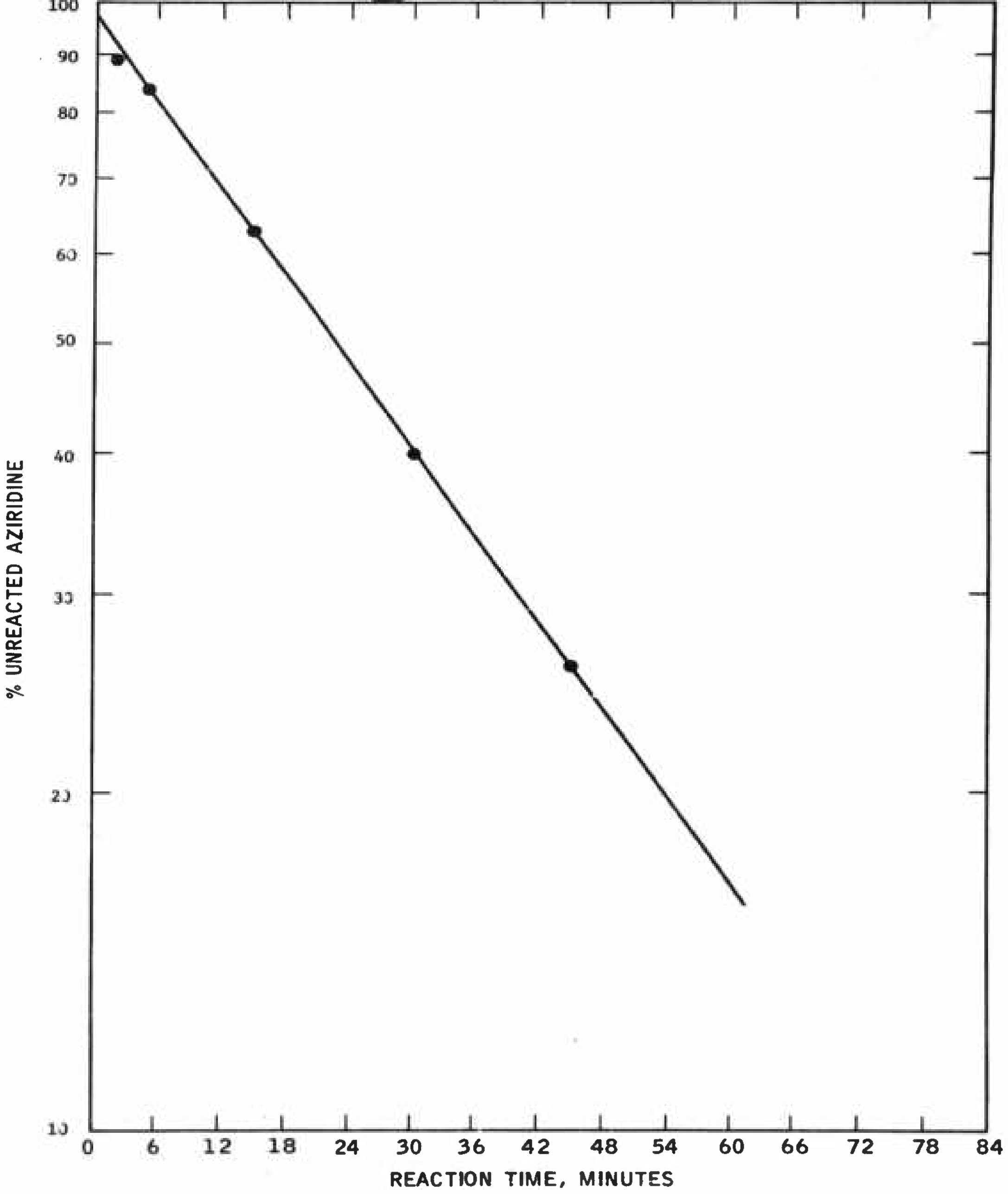
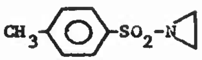
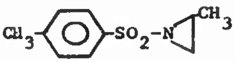
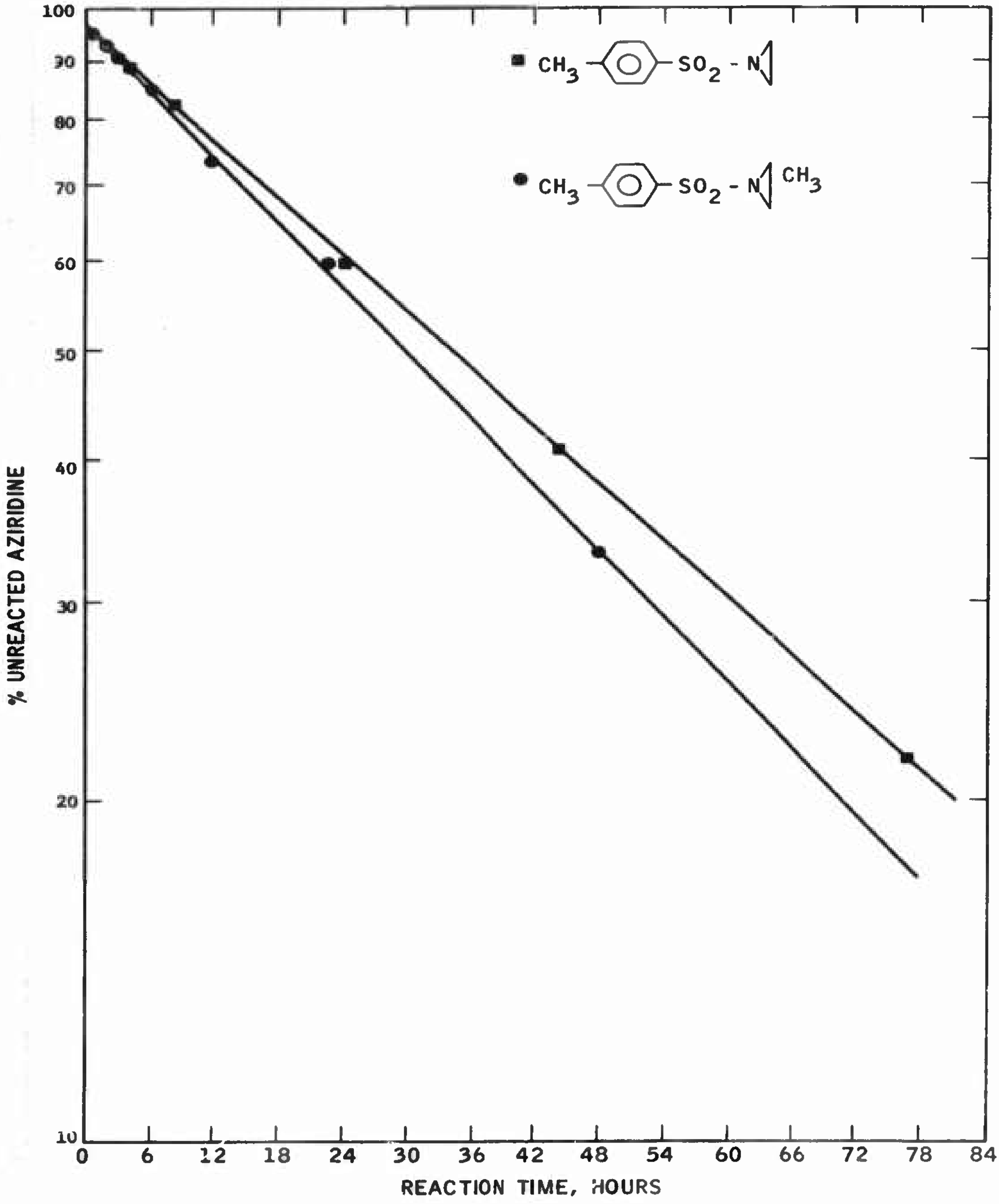


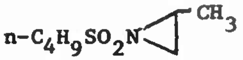
FIGURE 7

REACTION OF  AND  WITH EXCESS ACETIC ACID AT 50°C

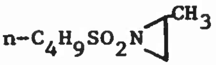


b. N-Butyl Sulfonyl Aziridine

The butane sulfonyl derivative of monomethyl sulfonyl aziridine,



, which is a liquid at room temperature, showed even lower reactivity with octanoic acid than N-aryl monomethyl sulfonyl aziridines. When reacted neat at 250°F with octanoic acid it required 2-3 days for complete reaction of the aziridine. Titration of the product still showed the presence of 17% of unreacted acid. The alkyl sulfonyl aziridine therefore offers no advantage in reactivity or stoichoimetry of reaction over N-aryl sulfonyl aziridines. The percentages of residual octanoic acid found by base titration after reaction of the aziridine at 250°F are shown below:

Aziridines	Reaction Time @ 250°F, Hrs.	% Unreacted Octanoic Acid
	17 (Incomplete)	51.9
	65	17.2

2.2. 2,2-Dimethyl Sulfonyl Aziridines

As pointed out previously, three N-aryl 2,2-dimethyl aziridines and one N-alkyl 2,2-dimethyl monofunctional sulfonyl aziridine were synthesized for kinetic evaluation. In addition a trifunctional curative, 1,3,5-tris(2,2-dimethyl aziridine-N-sulfonyl)benzene was synthesized to compare its reactivity and selectivity with that of the monofunctional analogue. Our studies with both N-aryl and N-alkyl sulfonyl aziridines are summarized in the following two sections.

a. N-Aryl-2,2-Dimethyl Sulfonyl Aziridines

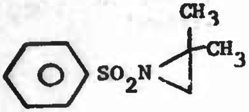
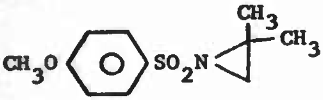
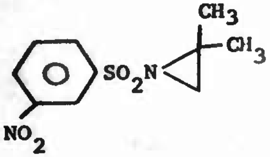
The reactivity of three N-aryl 2,2-dimethyl sulfonyl model aziridines with octanoic acid was determined at 150°F. At this temperature complete disappearance of the aziridine ring is observed in less than 24 hours. This improved reactivity of the 2,2-dimethyl aziridine as compared to the mono- and nonsubstituted sulfonyl aziridine was very encouraging. It suggested that 2,2-dimethyl aziridines could be used as potential curing agents within the practical range of propellant cure conditions.

Base titration of the unreacted octanoic acid, after complete reaction of the aziridine, however, showed consistently high percentages of unreacted octanoic acid (60-70%). Table IX summarizes the results for the three monofunctional 2,2-dimethyl aziridines when reacted neat with stoichiometric quantities of octanoic acid. All samples were titrated after complete reaction of the aziridine as evidenced by IR.

Table IX

REACTION OF 2,2-DISUBSTITUTED ARYL AZIRIDINES WITH OCTANOIC ACID

(Acid analysis after complete reaction of the aziridine)

Aziridine	Reaction Condition (°F/Days)	Acid Recovery, %
	150/4	61.0
	133/7	61.4
	150/4	69.5
	150/4	67.4
	150/6	65.5
	150/4	75.8

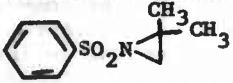
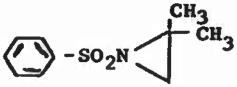
Our subsequent effort was directed towards selectively forming the desired addition product by studying the reactions in solution, in the presence of potential catalysts. Solution studies were carried out at 150°F in o-dichlorobenzene in the presence of zirconium acetyl acetonate. In general, the reactions in solution are slower than those carried out neat, but reasonable reaction rates were obtained by using zirconium acetyl acetonate as catalyst. Figure 8 shows the reaction profile for the reaction of  with octanoic acid. Reactions were monitored by infrared measurements by following the decrease in absorbance at 10.7μ representing the aziridine ring, and using the 3.45μ (C-H) band or the sulfonyl absorption band at 7.58μ as an internal reference. Matching cells were used to compensate for solvent absorption. As shown in Table X selectivity of the reaction was apparently not affected. The final product contained again large quantities of unreacted octanoic acid.

Table X

ACID RECOVERY AFTER REACTION WITH 2,2-DIMETHYL-AZIRIDINE-N-SULFONYL BENZENE



Concentration in o-Dichlorobenzene (wt. %)	Catalyst		Reaction Temp./Time	Acid Recovery (wt. %)
	Type	Wt. %		
Neat	None	--	150°F/4 Days	61.0
21.4	Zr(AcAc)$_4$	5	150°F/5.75 Days	72.4
		--	plus 250°F/2 Days	61.8
21.4	AlCl$_3$	2	150°F/5.75 Days	88.3

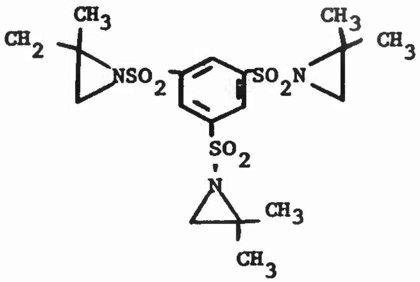
$AlCl_3$ and $FeCl_3$ were also tested to determine whether selectivity towards the desired sulfonamide ester could be improved. These materials were found to participate directly in the reaction rather than acting merely as catalysts. Apparently, both the $AlCl_3$ and $FeCl_3$ reacted with octanoic acid generating HCl which subsequently reacted rapidly with the aziridine.

All monofunctional 2,2-dimethyl sulfonyl aziridines had exhibited acceptable reactivity but poor selectivity to form the desired end product. It was of particular interest to determine whether a trifunctional analogue would show similar behavior with respect to both reactivity and selectivity. We therefore synthesized 1,3,5-tris(2,2-dimethyl aziridine-N-sulfonyl)benzene and compared its reactivity with that of the corresponding monofunctional aziridine. The reaction profile of this trifunctional aziridine with octanoic acid at 150°F in solution (o-dichlorobenzene) is shown in Figure 9. Comparison of Figures 8 and 9 shows that the mono- and trifunctional aziridine have similar reactivity. This lends support to our supposition that model compounds will adequately reflect the reactivity of the corresponding di- and trifunctional analogues.

Table XI also shows that the trifunctional 2,2-dimethyl aziridine is plagued by the same problem as the monofunctional 2,2-dimethyl aziridines; large amounts of unreacted acid remain after complete reaction of the aziridine. In at least one case heating at elevated temperatures appeared to have regenerated more acid. Subsequent analyses of the reaction products from 2,2-dimethyl aziridines as discussed later showed that the unsaturated sulfonamide(β-methallyl sulfonamide) was formed as a substantial by-product. Formation of the β-methallyl sulfonamide would regenerate the carboxylic acid and hence explain the large quantity of unreacted acid found after complete reaction of the aziridine.

TABLE XI

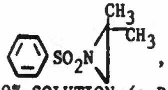
ACID RECOVERY AFTER REACTION WITH 1,3,5-TRIS-(2,2-DIMETHYL AZIRIDINE-N-SULFONYL) BENZENE



Concentration in O-Dichlorobenzene (wt. %)	Catalyst		Reaction Temp./Time	Acid Recovery (wt. %)
	Type	Wt. %		
Neat	None	--	150°F/60 hrs	54.4
18.8	$Zr(AcAc)_4$	5	150°F/5.75 Days	34.6
		--	plus 250°F/2 Days	66.2
18.8	$Zr(AcAc)_4$	5	R.T./5 Days	31.2
18.8	$FeCl_3$	2	R.T.	58.2
18.8	$AlCl_3$	2	R.T.	76.3

FIGURE 8

N-BENZENESULFONYL-2,2-DIMETHYL AZIRIDINE,


, WITH OCTANOIC ACID AT 150°F

IN 20% SOLUTION (o-DICHLOROBENZENE) WITH 5% Zr(AcAc)$_4$

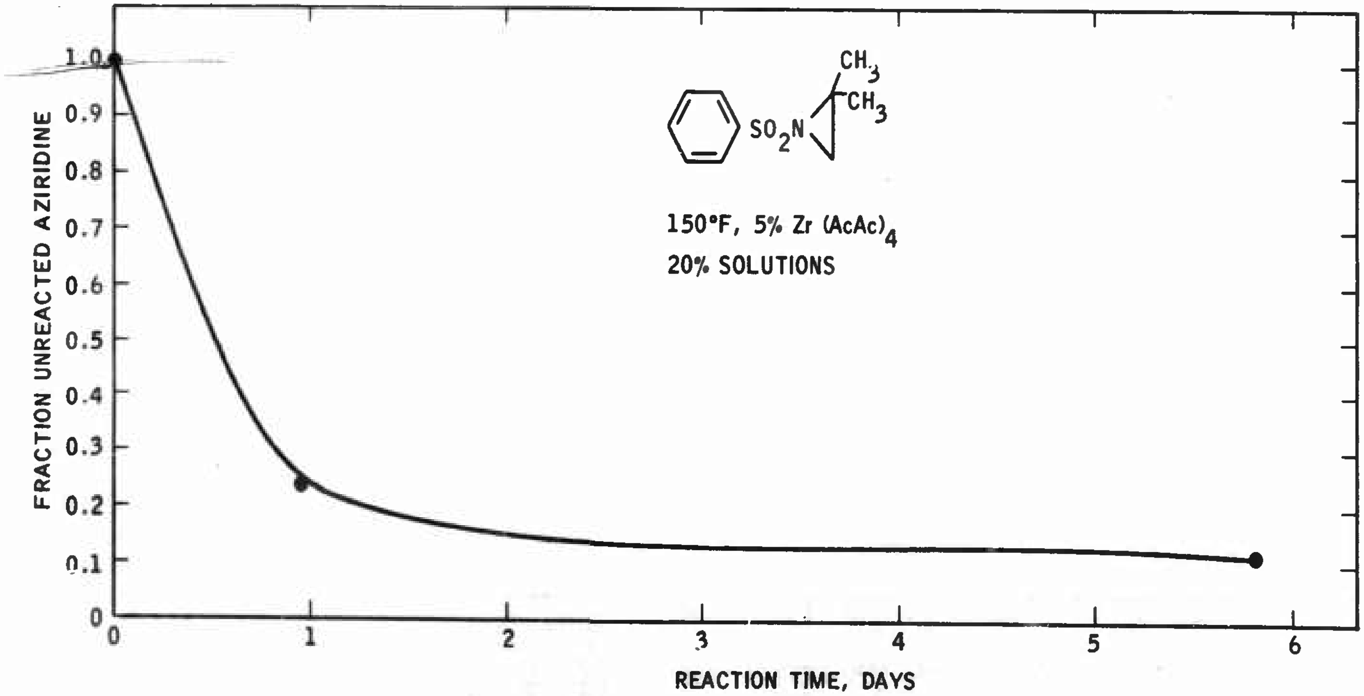
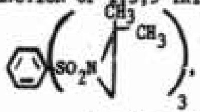
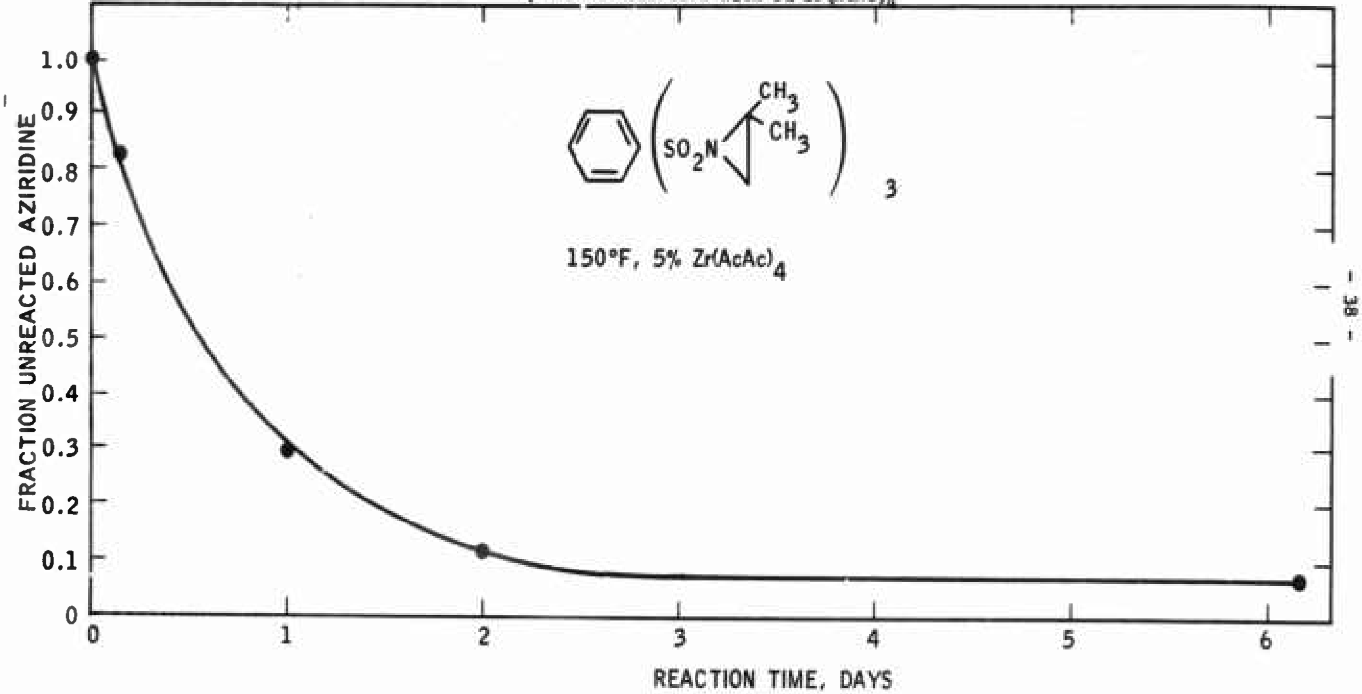


FIGURE 9

REACTION OF 1,3,5-TRIS(2,2-DIMETHYL AZIRIDINE-N-SULFONYL)BENZENE,  , WITH OCTANOIC ACID AT 150°F IN 20% SOLUTION (o-DICHLOROBENZENE WITH 5% $Zr(AcAc)_4$



b. N-Butyl Sulfonyl Aziridine

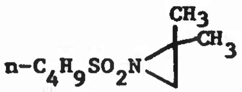
The butane sulfonyl derivative of 2,2-dimethyl sulfonyl aziridine was prepared to compare its reactivity with that of N-[aryl sulfonyl]aziridines.

The-2,2 disubstituted butane sulfonyl aziridine was considerably more reactive than the monosubstituted aziridine. This parallels the activity of the corresponding N-aryl sulfonyl aziridine indicating again that substitution on the aziridine ring dominates reactivity. For instance, the 2,2-dimethyl aziridine reacts at 150°F in 1-2 days whereas the monomethyl aziridine required more than 1 day at 250°F for complete reaction of the aziridine. The percentages of unreacted octanoic acid after complete reaction of the aziridine also paralleled the results from the reaction studies of N-aryl sulfonyl aziridines. The 2,2-dimethyl aziridine gave consistently high percentages of unreacted octanoic acid. Lowering the reaction temperature does not alter the product significantly as shown in Table XII. The rate of reaction is quite temperature sensitive as seen by comparing Figure 10 (133°F) with Figure 11 (110°F).

All information obtained to date shows that 2,2-dimethyl sulfonyl aziridines, both aromatic and aliphatic, exhibit good reaction rates but give undesirable products. Characterization of reaction products as discussed later showed that 2,2-dimethyl sulfonyl aziridines form unsaturated sulfonamide as well as the desired sulfonamide ester. Because of this, work with the 2,2-dimethyl sulfonyl aziridines was terminated.

TABLE XII

ACID RECOVERY AFTER REACTION WITH n-BUTYL SULFONYL (2,2-DIMETHYL AZIRIDINE-1) AT DIFFERENT TEMPERATURES



(Neat)

Reaction Temperature (°F)	Reaction Time (Days)	Acid Recovery (%)
150	1	52.4
150	2	43.8
133	7	46.1
110	26	42.1

FIGURE 10

REACTION OF N-[n-BUTANESULFONYL]-2,2-DIMETHYL AZIRIDINE WITH OCTANOIC ACID, NEAT AT 133°F

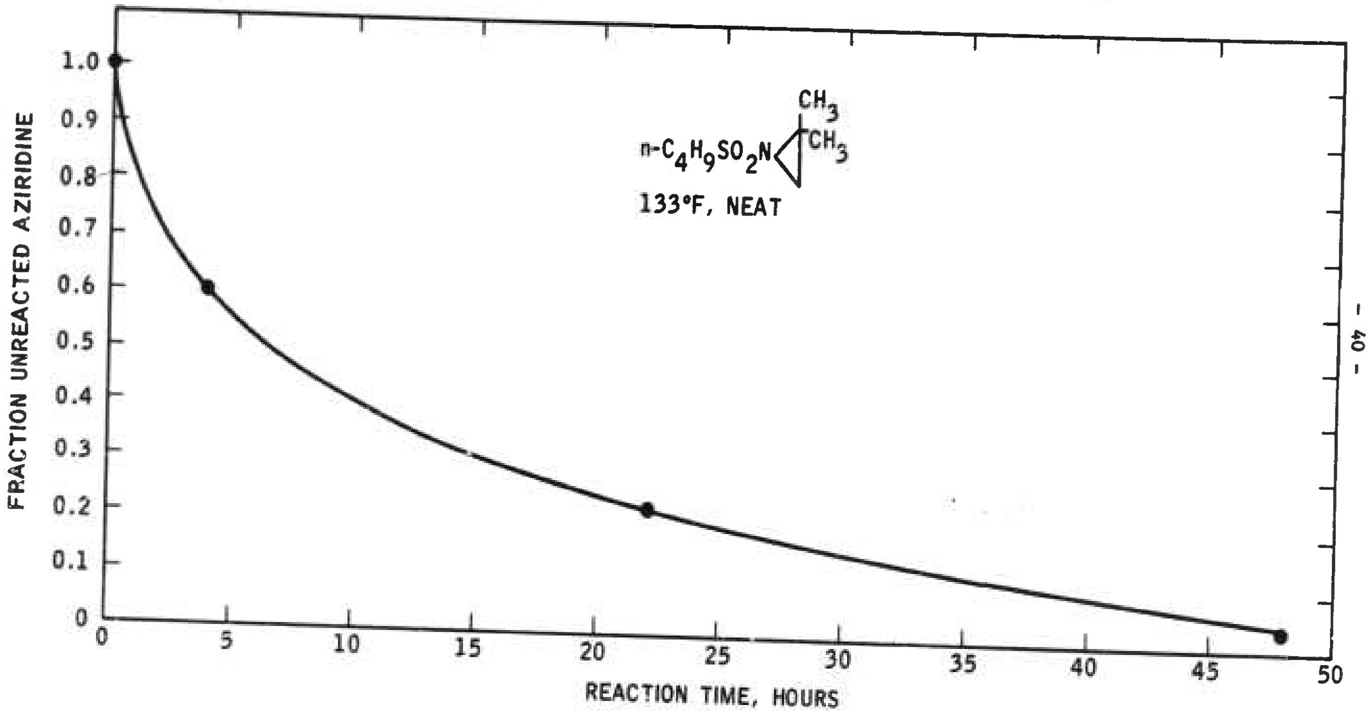
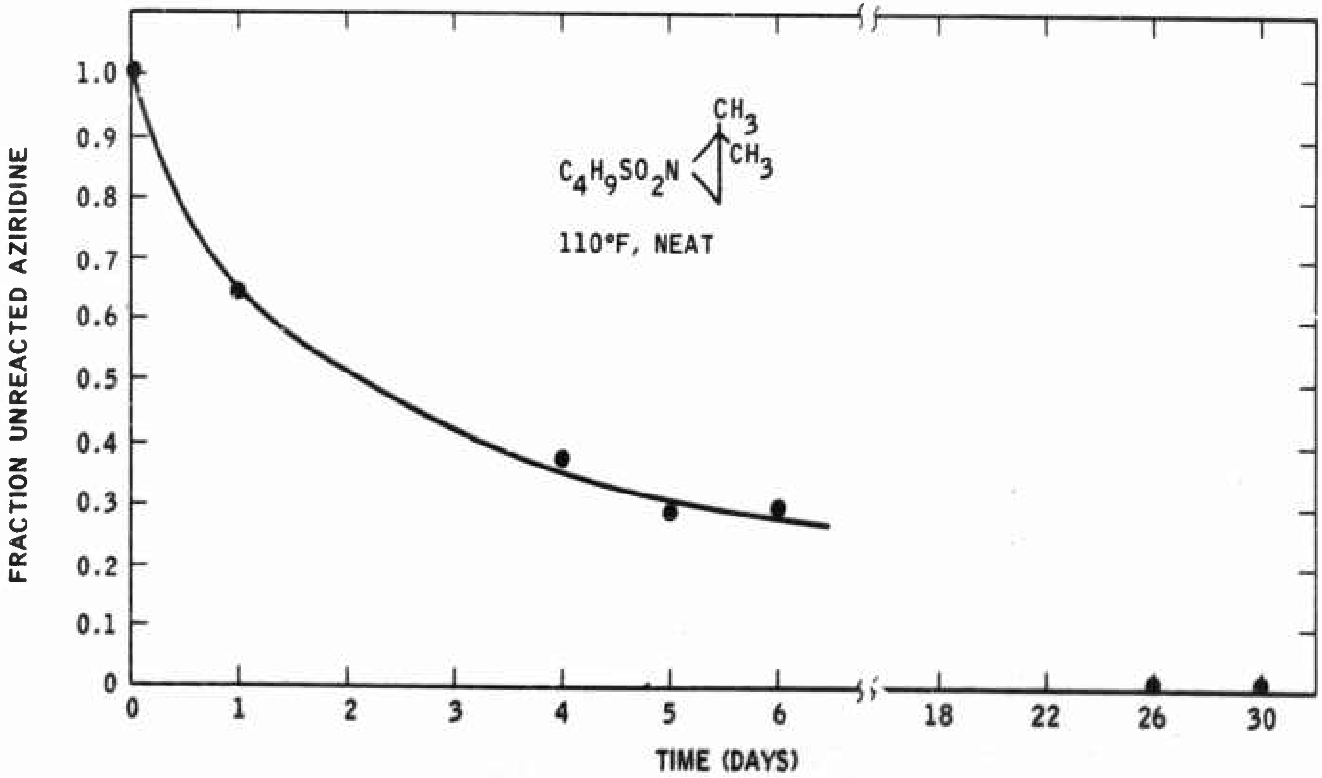


FIGURE 11

REACTION OF N-[n-BUTANESULFONYL]-2,2-DIMETHYL AZIRIDINE WITH OCTANOIC ACID, NEAT AT 110°F



2.3. N-Aryl 2,3-Dimethyl Sulfonyl Aziridine

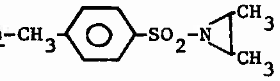
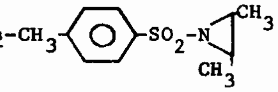
a. Acetic Acid Studies

Rate studies were carried out with *cis*- and *trans*- N-[p-toluenesulfonyl]-2,3-dimethylaziridine in excess acetic acid at 50°C (122°F). The reactions were followed by titrating the remaining aziridine with perchloric acid in the presence of tetrabutyl ammonium iodine. The results show that the reaction is psuedo first order and that the *trans*-derivative reacts faster than the *cis*. Figure 12 shows the rate profile for the *trans*-derivative and Figure 13 shows the rate profile for the *cis*-derivative.

A comparison of the half-lives for the reaction of the *cis*- and *trans*-isomers is given below.

TABLE XIII

REACTION OF cis- AND trans-N-[p-TOLUENESULFONYL]-2,3-DIMETHYL AZIRIDINES WITH EXCESS ACETIC ACID AT 50°C

Aziridine	$t_{1/2}$
cis- 	42.5 hours
trans- 	2 hours

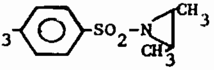
While the *trans*-derivative reacts considerably faster than the *cis*- it is still relatively slow compared to the 2-phenyl derivative and quite slow in comparison to the reactivity of HX-868.

b. Octanoic Acid Studies

Rate studies have been carried out with octanoic acid and *cis*- and *trans*-N-[p-methoxyphenylsulfonyl]-2,3-dimethylaziridine. The reaction profile with octanoic acid at 150°F, neat is shown in Figure 14. The *cis*-isomer appears to be more reactive than the *trans*, but the 2,3-dimethyl aziridines are less reactive than the corresponding monomethyl aziridine. The reaction product of the *cis*-isomer with octanoic acid was titrated with base when aziridine analysis by IR showed that 15% of the aziridine remained unreacted. Titration showed that 11% of the acid was still unreacted. These data in conjunction with IR spectra show that the desired addition reaction is taking place and that no significant amount of homopolymerization is encountered.

The difference noted in the relative rates of the *cis*- and *trans*-isomers in acetic acid and octanoic acid is not understood at this time and further work will be done to find an explanation.

FIGURE 12

REACTION OF trans-CH_3- WITH EXCESS ACETIC ACID AT 50°C

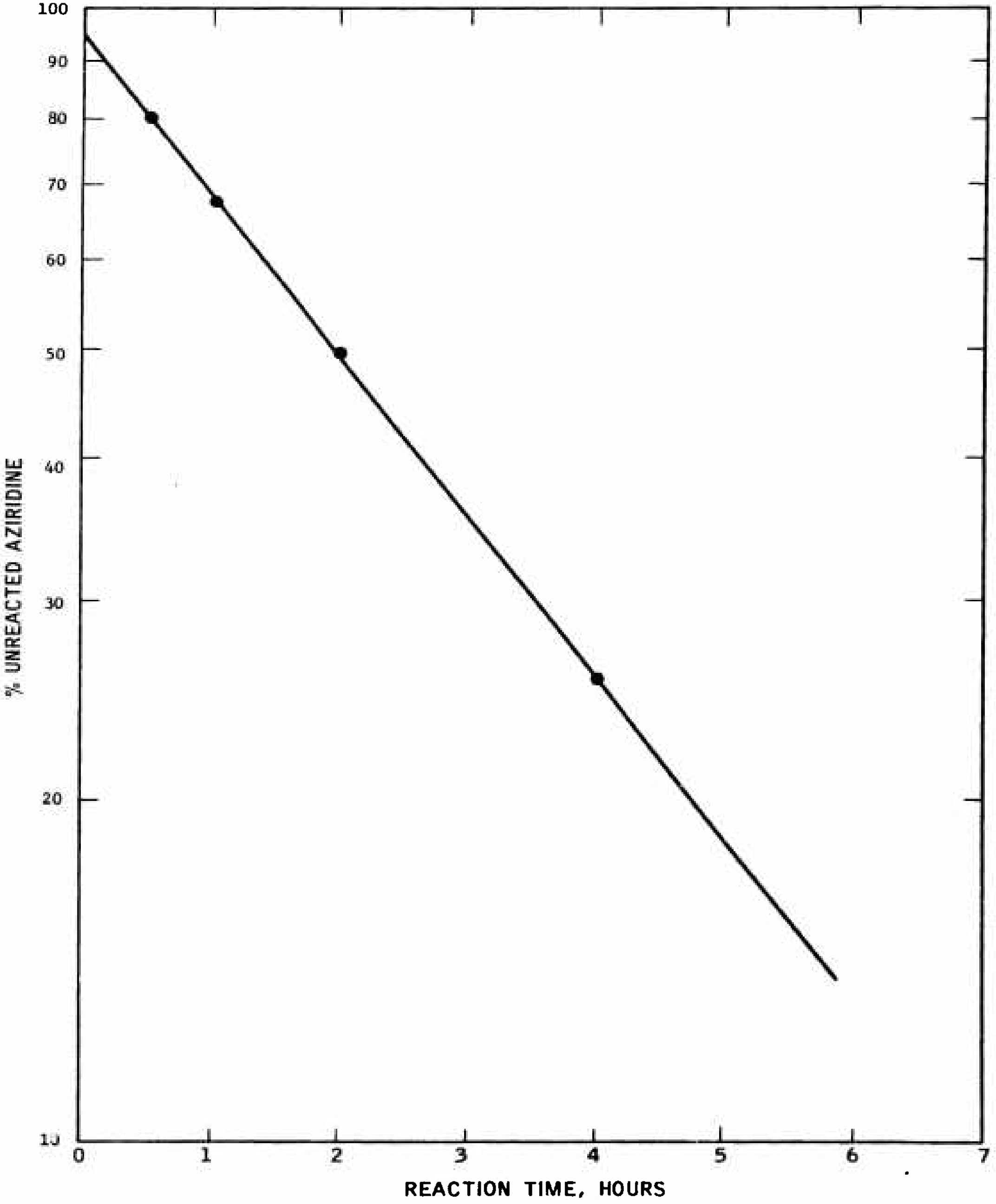
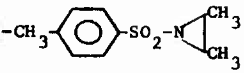


FIGURE 13

REACTION OF cis- 

WITH EXCESS ACETIC ACID AT 50°C

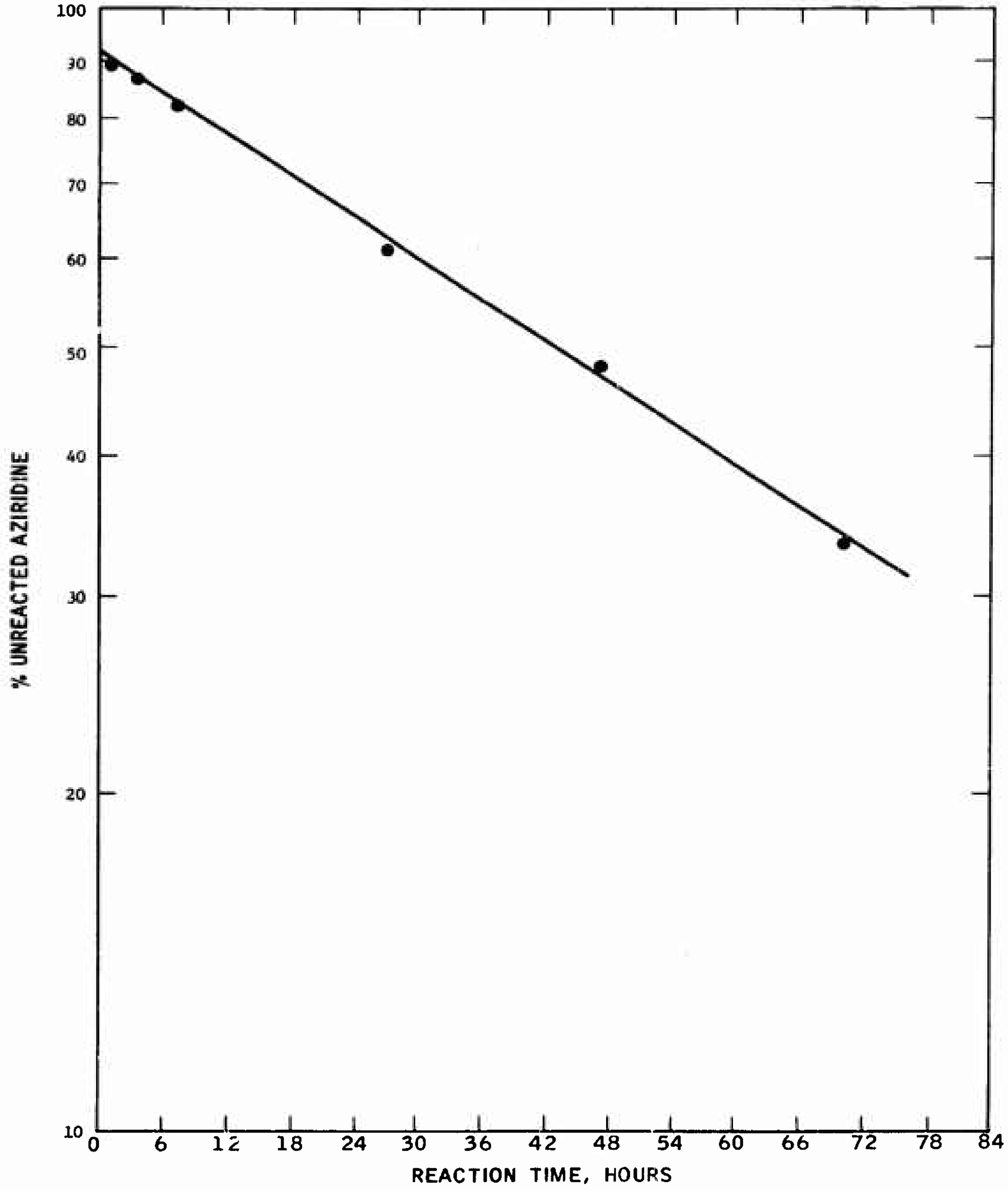
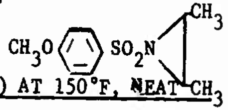
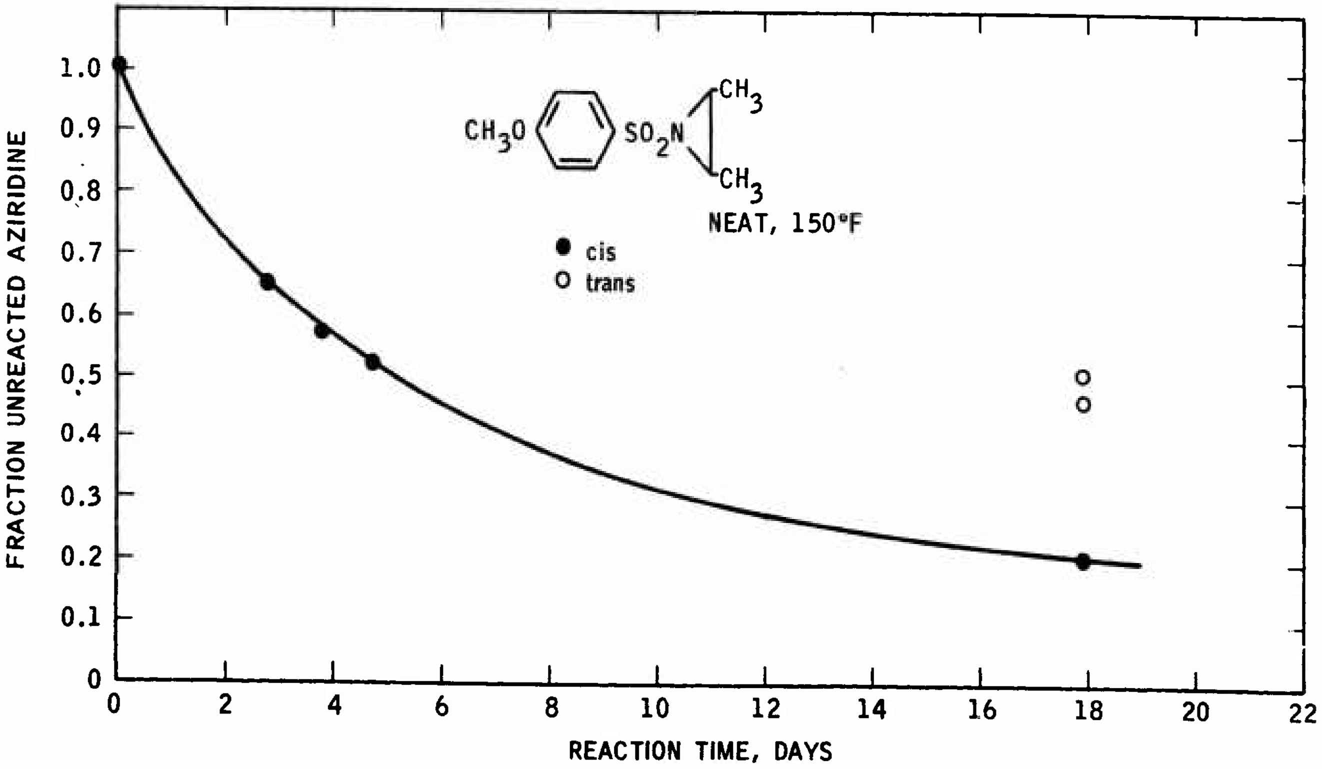


FIGURE 14

REACTION OF CIS- AND TRANS-  WITH OCTANOIC ACID (1/1) AT 150°F, NEAT



c. Catalyst Studies

The reaction of 2,3-dimethyl sulfonyl aziridines with acids appears to be very selective with little or no side reaction. However, the rate of reaction is quite slow and for these materials to be considered as curatives for propellants the cure rate must be improved.

Zirconium acetyl acetonate has been reported in the literature as having catalytic activity for the aziridine-acid reaction, so this material was examined as a catalyst for the 2,3-dimethyl sulfonyl aziridine-octanoic acid reaction. It appeared to have moderate catalytic activity but its effect was still too low for practical application in propellant binders.

Subsequently, a total of 15 different acetyl acetonates were examined as catalysts for the aziridine-acid reaction, but none of these materials showed reasonable catalytic activity. Among the catalysts tried were aluminum, beryllium, cobalt, chromium, copper, ferric, manganese, nickel, titanium, vanadium, and vanadyl acetyl acetonates.

Studies with BF_3 etherate as a catalyst were conducted to determine both the selectivity of the catalyst and the effect on the rate of reaction. In the case of N-[p-toluene sulfonyl]-2-methyl aziridine the selectivity appeared to be quite low when BF_3 etherate was used as a catalyst. It was felt that the major competing reaction was homopolymerization of the aziridine and it was previously shown that 2-methyl aziridine did react in the presence of BF_3 etherate. To check the extent of homopolymerization the rate of disappearance of aziridine in the presence of BF_3 etherate was examined. Table XIV gives the extent of disappearance of aziridine for several 2,3-dimethyl and 2-methyl aziridine derivatives.

TABLE XIV

REACTION OF 2,3-DIMETHYL AND 2-METHYL SULFONYL AZIRIDINES WITH BF_3 ETHERATE

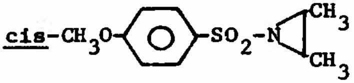
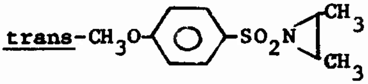
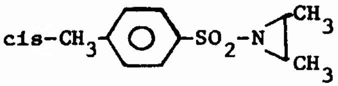
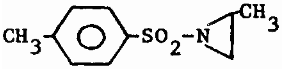
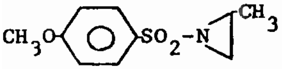
Aziridine	BF_3 Etherate Wt% on Aziridine	Reaction Time Hrs.	Unreacted Aziridine, %
	3.3	96	96.8
	2.7	96	94.7
	3.1	96	84.0

TABLE XIV (Cont'd)

Aziridine	BF_3 Etherate Wt% on Aziridine	Reaction Time Hrs.	Unreacted Aziridine, %
	3.6	96	84.0
	3.3	96	69.3

After 4 days there appears to be very little side reaction with the 2,3-dimethyl aziridines. The mono-methyl derivative on the other hand showed more extensive side reaction.

The effect of the BF_3 etherate catalyst on selectivity of the acid reaction with 2,3-dimethyl aziridine was examined in both ether and toluene. Both cis- and trans-N-[p-methoxy-phenylsulfonyl]-2,3-dimethyl aziridine were reacted with octanoic acid in ether in the presence of BF_3 etherate. As shown below, there was good selectivity with the cis-derivative (12.3% unreacted acid after 21 hours) but poor selectivity with the trans-derivative (53.5% unreacted acid after 20 hours).

TABLE XV.

REACTION OF cis- AND trans-N-[p-METHOXYPHENYLSULFONYL]-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID IN THE PRESENCE OF $BF_3 \cdot OEt_2$(1)

	Cis-Derivative	Trans-Derivative
Reaction Time, hours	21	20
Unreacted Acid, %	12.3	53.5

---

(1) 20% concentration in ether; 1:1 aziridine/acid; 0.4% $BF_3 \cdot OEt_2$; room temperature. Ether was removed by evaporation and IR spectrum taken in o-dichlorobenzene showed reactions were completed. Acid titration was done in chloroform.

The effect of the BF_3 etherate catalyst on the cis-2,3-dimethyl derivative was also examined in toluene. The reaction was complete within one hour, as evidenced by the disappearance of the aziridine by IR. The selectivity was excellent with only 1.3% acid remaining when 0.2% BF_3 etherate was used and 6.5% acid remaining when 2% BF_3 etherate was used. The results are summarized in Table XVI.

TABLE XVI

REACTION OF cis-N-[p-METHOXYPHENYLSULFONYL]-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID IN THE PRESENCE OF $BF_3 \cdot OEt_2$ IN TOLUENE(1)

$BF_3 \cdot OEt_2$ Concentration, %	0.2	2
Reaction Time, Hours	1	1
Unreacted Acid, %	1.3	6.5

---

(1) 20% concentration in toluene; 1:1 aziridine/acid; room temperature

While the selectivity of the reaction is quite good the rate of reaction is too rapid for practical use. Lower catalyst concentrations were used to see if the reaction could be slowed to a more manageable rate. As shown below the rate can be slowed considerably but BF_3 etherate does not appear to be a practical catalyst for propellant mixes.

TABLE XVII

REACTION OF cis- AND trans-N-[p-METHOXYPHENYLSULFONYL]-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID(1)

	Cis-Derivative	Trans-Derivative
BF_3 Etherate, %	0.16	0.35
Reaction Time, Hrs.	65	48
Unreacted Aziridine, %	15.1	0
Unreacted Acid, %	17.4	29.4

---

(1) 20% concentration in toluene; 1:1 aziridine/acid; room temperature

At these lower catalyst levels the <u>trans</u>-derivative appears to react faster than the <u>cis</u> based on disappearance of aziridine in the infrared spectra. However, the indications are that the <u>trans</u> undergoes some side reactions while the <u>cis</u> is quite selective.

It is clear that the rate of reaction is too fast with BF_3-etherate as the catalyst. However, the feasibility of pursuing the catalyst study for improving the rate of reaction for the sulfonyl aziridines has been demonstrated. The reaction selectivity is good and it now becomes a question of finding a catalyst which gives a more suitable rate of reaction.

One approach is to cut down the reactivity of BF_3 with a stronger complex. This was done with a BF_3·tributylphosphate complex. At a 0.2 weight percent concentration this catalyst proved to be too slow in catalyzing the reaction of _cis_- and _trans_-N-[p-methoxyphenylsulfonyl]-2,3-dimethyl aziridine with octanoic acid. After 28 hours at room temperature only 15% of the _cis_- and 10% of the _trans_-aziridine derivatives had reacted. Even after an additional 70 hours at _150°F_ only 21% of the _cis_- and 17% of the _trans_-derivatives had reacted. After 22 days at _150°F_ only 25% of the _aziridine_ had reacted.

At a BF_3·tributylphosphate concentration of 0.6 weight percent the catalyst appeared to be too rapid as shown in Table XVIII. The _cis_-2,3-dimethyl aziridine reacted completely within 22 hours while the _trans_-derivative was slower but still fairly reactive.

TABLE XVIII

REACTION OF cis AND trans-N-[p-METHOXYPHENYL SULFONYL]-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID IN THE PRESENCE OF $BF_3 \cdot (BuO)_3PO[1/1]^{(1)}$

Aziridine	Wt% Catalyst	Reaction Time	% Unreacted Aziridine
cis-derivative	0.69	22 hours	0
	0.24	28 hours	85
trans-derivative	0.62	22 hours	38.2
	0.24	28 hours	90

---

(1) 20% concentration in toluene; 1:1 aziridine/acid; room temperature

With this particular catalyst the catalytic activity can be adjusted by varying the ratio of BF_3 to tributylphosphate.

A series of catalysts with varying $BF_3/(BuO)_3PO$ ratios was examined at 120°F. These results are summarized below.

TABLE XIX

REACTION OF cis-N-[p-TOLUENESULFONYL]-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID IN THE PRESENCE OF $BF_3\cdot(BuO)_3PO$ CATALYSTS AT 120°F

Ratio $BF_3/(BuO)_3PO$	Wt% Catalyst	Wt% BF_3 Based on Aziridines	Reaction Time	% Unreacted Aziridines
1/1	0.5	0.8	5 days	60.3
0.75/1	0.4	0.53	5 days	76.8
0.50/1	1.1	1.06	5 days	17.1
0.25/1	1.0	0.49	5 days	68.0

At the lower levels of catalyst the reaction appears to level off after about 6 hours and not much more reaction occurs up to 6 days. The 0.50/1 $BF_3\cdot(BuO)_3PO$ catalyst at a level of 1.6% gave the reaction profile shown in Figure 15. This reaction appears to be relatively well controlled but may still be a little too fast in the initial stages.

The addition reaction was also examined at a higher concentration of the 0.75 BF_3/1 $(BuO)_3PO$ complex. Figure 16 shows the rate of disappearance of aziridine in the reaction of cis-N-[-p-toluenesulfonyl]-2,3-dimethyl aziridine with octanoic acid in the presence of 0.8% of this catalyst. The reaction appears to be much more controlled, although again the initial rate may still be a little too rapid.

Two other BF_3 complexes were examined as catalysts. A $BF_3\cdot$piperidine complex showed no activity at concentrations of 0.5 and 1.7 percent. A $BF_3\cdot$diphenyl amine complex had activity as shown below, but does not appear to be a satisfactory catalyst because of poor selectivity.

TABLE XX

REACTION OF cis-N-[p-TOLUENESULFONYL]-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID IN THE PRESENCE OF $BF_3\cdot$DIPHENYL AMINE(1)

Catalyst Concentration Weight %	Reaction Time	% Unreacted Aziridine	% Unreacted Acid
0.75	2 hours	10	38
0.53	4 hours	10	29
0.36	24 hours	44	78
	48 hours	41	--
0.15	4 days	85	--

---

(1) 20% concentration in toluene; 1/1 aziridine/acid; 120°F.

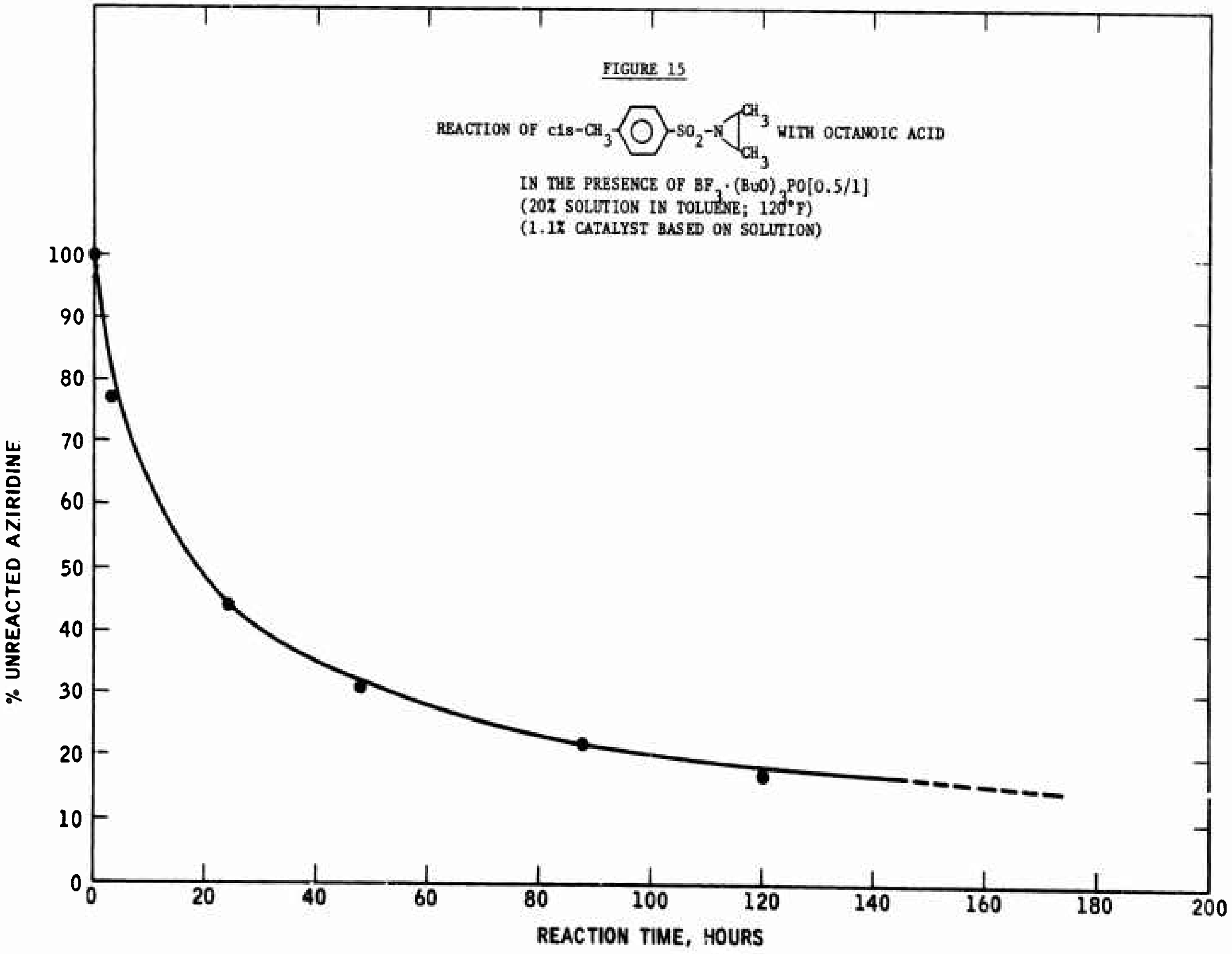


FIGURE 15

REACTION OF cis-$CH_3-C_6H_4-SO_2-N(CHCH_3)_2$ WITH OCTANOIC ACID

IN THE PRESENCE OF $BF_3\cdot(BuO)_3PO$[0.5/1]
(20% SOLUTION IN TOLUENE; 120°F)
(1.1% CATALYST BASED ON SOLUTION)

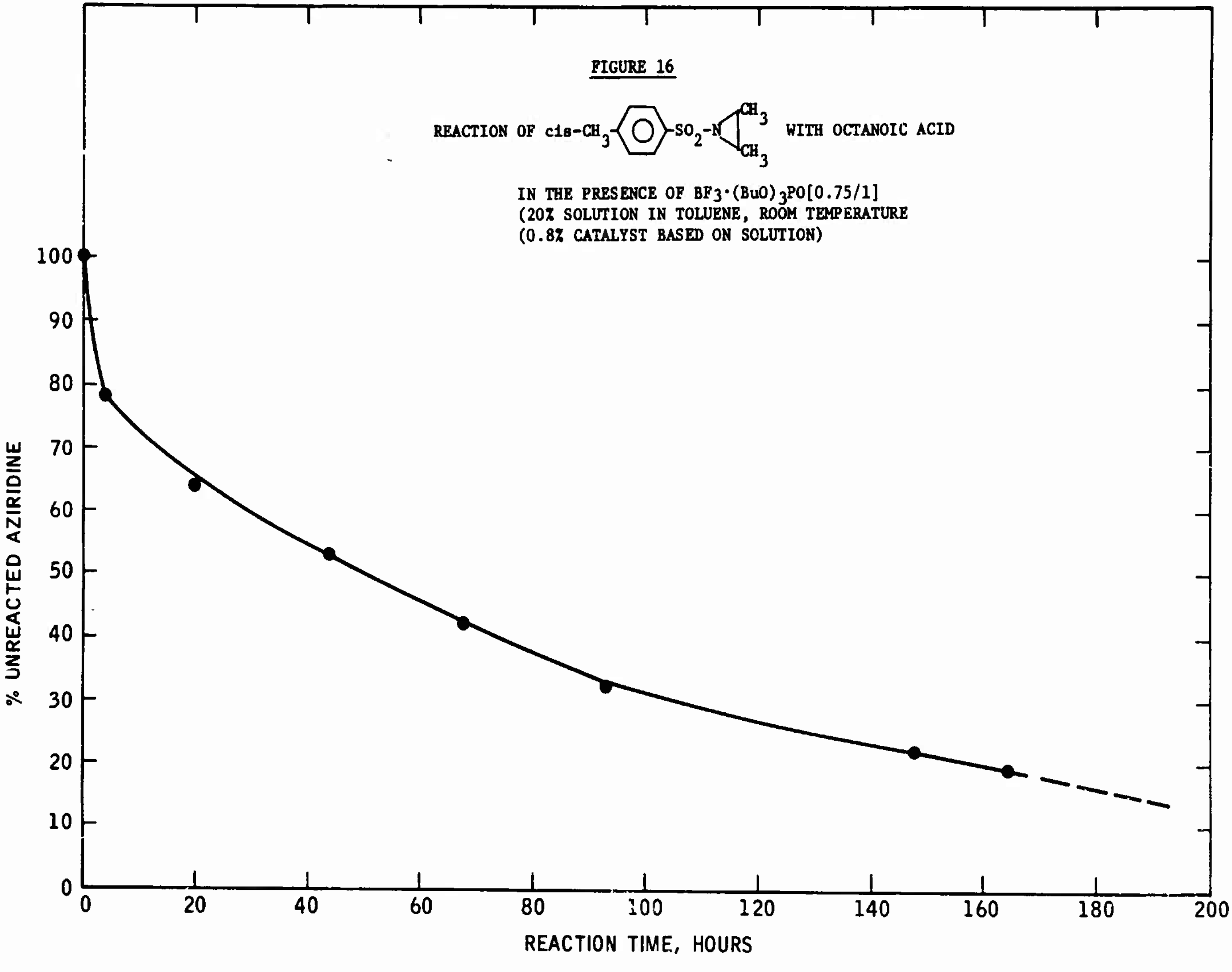


FIGURE 16

REACTION OF cis-CH_3- -SO_2-N CH_3 CH_3 WITH OCTANOIC ACID

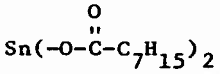
IN THE PRESENCE OF $BF_3 \cdot (BuO)_3PO$[0.75/1]
(20% SOLUTION IN TOLUENE, ROOM TEMPERATURE
(0.8% CATALYST BASED ON SOLUTION)

The rate of reaction appears to be very sensitive to the catalyst level and is not particularly selective. No further work was done with this catalyst because of these factors.

A series of tin compounds was examined for activity in the reaction of <u>cis</u>-N-[p-toluenesulfonyl]-2,3-dimethyl aziridine with octanoic acid. Tributyltin chloride, dibutyltin dichloride, and dibutyltin acetate showed no activity after seven days at 120°F. Butyltin trichloride showed very slight activity with 11% of the aziridine reacting in 4 days. With stannic chloride 45% of the aziridine had reacted within 4 days. However, with the stannic chloride 100% of the acid was recovered which indicates that none of the addition reaction occurred. These results are summarized below.

TABLE XXI

REACTION OF cis-N-[p-TOLUENESULFONYL]-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID IN THE PRESENCE OF TIN COMPOUNDS(1)

Compound	Weight %	Reaction Time Hours	% Unreacted Aziridine
Bu_2SnCl_2	0.6	7 days	100
$Bu_2Sn(OAc)_2$	1.0	7 days	100
Bu_3SnCl	1.8	7 days	100
 $Sn(-O-\overset{O}{\overset{\|}{C}}-C_7H_{15})_2$	1.1	4 days	100
$BuSnCl_3$	1.4	4 days	89
$SnCl_4$	1.4	4 days	55(2)

---

(1) 20% concentration in toluene; 1/1 aziridine/acid; 120°F.

(2) 100% acid recovered.

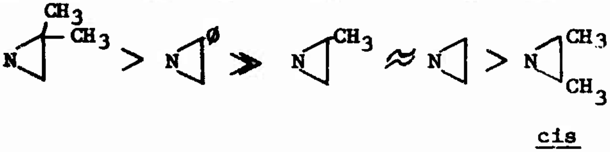
Several lithium based catalysts were examined also. Lithium stearate at a concentration of 1.3% showed no catalytic activity. Lithium perchlorate at a level of 1.8 had slight activity with 35% of the aziridine reacting in 10 days and 52% reacting in 16 days. Lithium tetrafluoroborate had greater activity with 73% of the aziridine reacting in 7 days and 82% reacting in 10 days. However, titration of the reaction mixture with base showed 50% of the acid remaining which indicates that 32% of the aziridine had reacted non-selectively. Both lithium perchlorate and lithium tetrafluoroborate look interesting enough to warrant further work.

Other compounds that were examined and showed no catalytic activity for the aziridine-acid addition reaction included aluminum chloride, aluminum isopropoxide, aluminum stearate, antimony tallate, antimony triacetate, cobalt octoate, ferric chloride, lead octoate, lithium t-butoxide, titanium tetrachloride sodium titanate, tetraisopropyl titanate, and zirconium tetrachloride.

The rate of reaction between monomethyl or 2,3-dimethyl sulfonyl aziridines and carboxylic acid is too slow in the absence of catalysts. BF_3 etherate make the reaction too fast. The $BF_3 \cdot$tributylphosphate complex appears promising, as does lithium tetrafluoroborate. Further work is needed to obtain the right catalyst at a proper level of catalytic activity.

3. Characterization of Reaction Products of Sulfonyl Aziridines With Carboxylic Acids

From rate studies of the reaction between sulfonyl aziridines and octanoic acid the order of reactivity has been found to be:

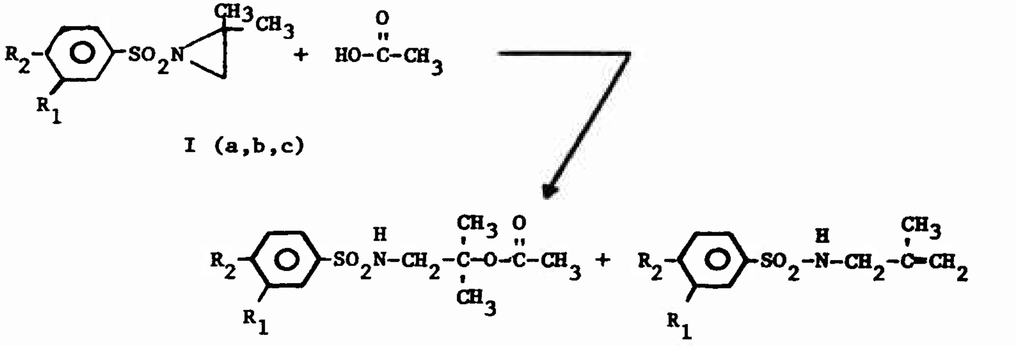


The reaction products were of interest because they might provide some insight into the probable role of steric and electronic effects towards ring opening rates and selectivity. Acid isolation and characterization of the ring opened product would be facilitated.

3.1. Reactions of 2,2-Dimethyl Sulfonyl Aziridines with Acetic Acid

Although the 2,2-disubstituted series appeared to be suitable from a rate standpoint, there was considerable octanoic acid left when all of the aziridine had been consumed.

The products from the reaction of 2,2-dimethyl sulfonyl aziridines and acetic acid have been identified according to the following equation:



I (a,b,c)

sulfonamide ester

II (a,b,c)

β-methallyl sulfonamide

III (a,b,c)

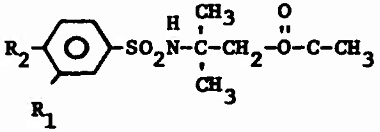
Where: a. when $R_1 = NO_2$, $R_2 = H$

b. when $R_1 = H$, $R_2 = CH_3$

c. when $R_1 = H$, $R_2 = OCH_3$

These products were separated by column chromatography. The isolated sulfonamide esters, IIa, IIb, and IIc, were identified by IR and NMR as the major products and the unsaturated sulfonamide, IIIa, IIIb, and IIIc, as the minor products.

NMR analysis of a mixture of products clearly differentiated between II and the alternate possibility IV which would arise from the so-called normal mode of addition of nucleophiles to the aziridines.



IV

Structure II is consistent with the proton picture which predicts a triplet for the nitrogen proton and a doublet for the methylene protons in the ratio of 1:2 (see Appendix C5). Structure IV would have yielded a singlet for N-H as well as for CH_2.

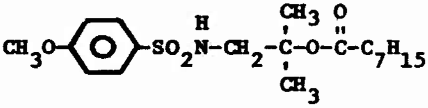
The presence of III (see Appendix C5 in the reaction mixture is suggested for the following reasons:

- The appearance of vinyl absorption in the 5.1 - 5.2τ region.
- A downfield shift of the methyl singlet due to α-vinyl substitutent.
- The splitting of the methylene into a doublet by the single hydrogen on the adjacent nitrogen.
- The splitting of the hydrogen on the nitrogen into a triplet by the adjacent methylene.
- The identity of the N-H and CH_2 coupling constants.

3.2. Reactions of 2,2-Dimethyl Sulfonyl Aziridine with Octanoic Acid

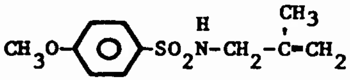
N-[p-methoxyphenyl sulfonyl]-2,2-dimethylaziridine and N-[n-butyl sulfonyl]-2,2-dimethylaziridine were reacted with octanoic acid. The NMR spectra of these reaction products are shown in Appendix C5. An NMR spectrum of octanoic acid is also shown in Appendix C5 to assist interpretation.

Comparing the NMR spectrum shown in Figure with Figures and and applying the same reasoning as mentioned in Section 1, we identified similar products for the reaction of N-[-p-methoxyphenyl sulfonyl]2,2-dimethyl aziridine as shown below.



V

+



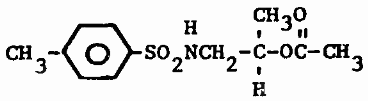
IIIc

In this case, products V and IIIC were estimated to be in equal molar quantities. This explains why 50 to 60% of octanoic acid in the reaction mixture remained as observed in the past after the aziridine had disappeared.

The 2,2-dimethyl substituent increases the reaction rate with carboxylic acid considerably when compared to the reaction rates for the 2-methyl and 2,3-dimethyl aziridine series, but selectivity is lost because of a fast competitive reaction to form the β-methallyl sulfonamide.

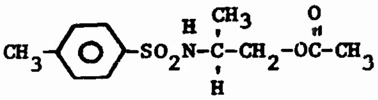
3.3. Reaction of Monomethyl Sulfonyl Aziridine with Acetic Acid

Only one product was obtained when N-[p-toluene sulfonyl]-2-methyl aziridine was heated in excess acetic acid. From spectral analysis either VI or VII was formed but no unsaturate was identified.



VI

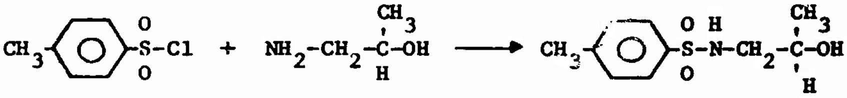
+



VII

Either product would be the desired reaction product. In kinetic studies with the 2-methylaziridine derivatives it has been found that little or no unreacted acid remains after the aziridine has reacted. A selective reaction between octanoic acid and monomethyl aziridines is therefore supported by both NMR spectra and kinetic data.

To distinguish between structures VI and VII, structure VI was synthesized by an unambiguous method; p-tolylsulfonyl chloride was reacted with 1-amino-2-propenol to give VIII followed by acetolysis with acetyl chloride to yield VI. Both the NMR and IR spectra of VI did not agree with the spectra obtained from the reaction product of N-[p-tolyl sulfonyl]-2-methyl aziridine and acetic acid. (See Appendix C5)



VIII

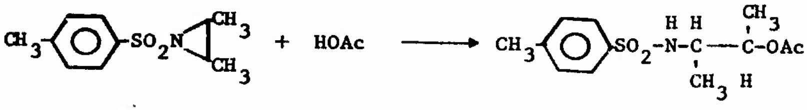
$$\text{VIII} + CH_3COCl \longrightarrow \text{VI}$$

3.4. Reaction of N-[p-Tolyl Sulfonyl]-2-Phenyl Aziridine with Acetic Acid

When N-[p-tolyl sulfonyl]-2-phenyl aziridine was heated with excess acetic acid the only product isolated was N-[2-acetoxy-2-phenyl ethyl]p-tolyl sulfonamide. The structure was confirmed by the NMR spectrum which showed a triplet for the amido proton.

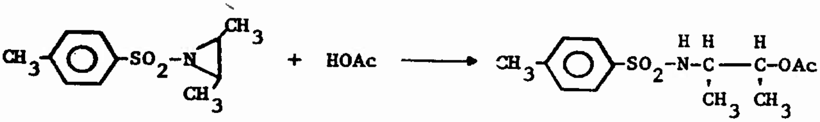
3.5. Reaction of N-[p-Tolyl Sulfonyl]-cis-2,3-Dimethylaziridine and N-[p-Tolyl Sulfonyl]-trans-2,3-Dimethyl Aziridine with Acetic Acid

Reaction between IX and X with excess acetic acid gave threo-XI and erythro-XII, respectively in nearly quantitative yields. Compound III and IV were consistant with elemental, I.R., and NMR analysis. Ring opening occurred with complete stereospecificity analogous to the ring opening reactions reported for cis- and trans-2,3-dimethyl aziridines and cis- and trans-2,3-dimethyl epoxides.



cis-IX

threo-XI

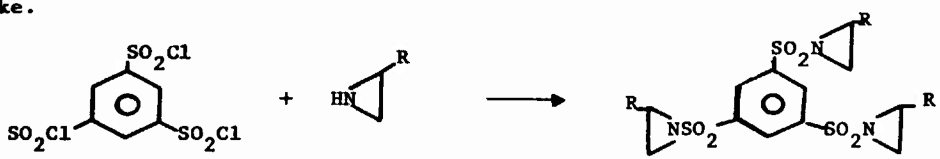


trans-X

erythro-XII

4. Synthesis of Di- and Trifunctional Curatives Based on Sulfonyl Aziridines

Tris-aziridine derivatives XIIIa,b from S-benzene sulfonylchloride and 2-methyl aziridine or 2-phenyl aziridine proved to be difficult to make.

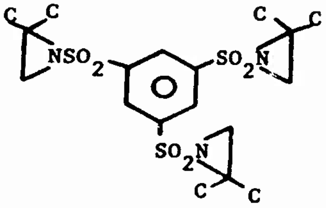


XIIIa, R=CH_3

XIIIb, R=phenyl

The products were inseparable mixtures resulting presumably during synthesis from nucleophilic opening of the aziridine ring. No improvement was observed in the product when the reaction was carried out in methylene chloride, carbon tetrachloride, tetrahydrofuran, or tetrahydrofuran-ether mixtures.

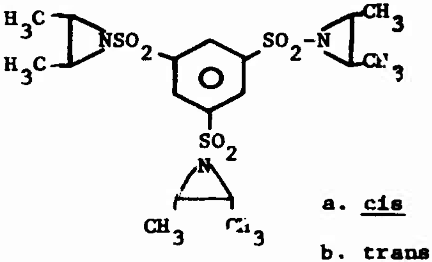
On the other hand, in THF the reaction between S-benzene trisulfonyl chloride and 2,2-dimethyl aziridine yielded XIV, m.p. 53.5-54°C.



XIV

Apparantly the tendency to undergo nucleophilic ring opening in THF is minimized when enough substitutents are placed on the ring.

Because N-(arylsulfonyl)-cis-2,3-dimethyl aziridine and the trans-2,3-dimethyl isomer appear to be promising from a rate and selectivity standpoint the preparation of the tri-substituted cis- and trans-2,3-dimethyl aziridine XVa,b was attempted. In tetrahydrofuran or tetrahydrofuran-ether mixtures product XVa was collected (m.p. 188-189°C). I.R. and NMR spectra are consistant with XVa No chlorine was detected with silver nitrate solution. The material was soluble in benzene and hot hexane. Elemental analysis was satisfactory. Product XVb collected in 8% yield was identified also by NMR and IR.



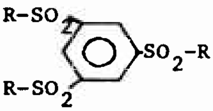
a. cis

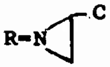
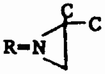
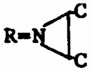
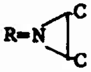
b. trans

XV

TABLE XXII

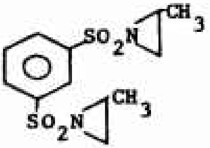
Trifunctional Curatives
Benzene-1,3,5-Tris (N-Sulfonyl Aziridines)



	m.p.	Yield	
	(a)	85	ether CH_2Cl_2 dichloroethane CCl_4 toluene THF acetonitrile
	53.5-54.0	82	THF
 cis	188-189	37	
 trans	122.5-123	8	

(a) impure

Difunctional sulfonyl aziridines were easily prepared from purified m-benzene sulfonyl chloride and the appropriate aziridine. The reaction between the ether soluble m-disulfonyl chloride and 2-methyl aziridine in ether solution gave XVI in 32% yield recrystallized from

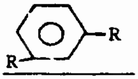
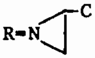
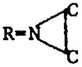


XVI

Esso hexane, m.p. 68-69°C. There appears to be no difficulty to make 2-methyl aziridinyl derivatives of m-disulfonyl chloride by this route. The cis-2,3-dimethyl aziridine counterpart was similarly made in relatively high purity; m.p. 140-141°C. An aziridine titration (Table XXIII) revealed a purity of ~ 97%.

TABLE XXIII

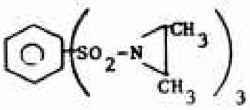
Difunctional Sulfonyl Aziridine Curatives
Benzene-1,3-Bis[N-Sulfonyl Aziridines]

	% Aziridine, by Titration[(a)]	m.p., °C	Yield, %
	--	68-69	32
 cis	97.0 ± .2	140-141	59

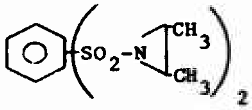
(a) Titrated by tetrabutyl ammonium iodide: perchloric acid method.

5. Evaluation of Di- and Trifunctional Curatives Based on Sulfonyl Aziridines

Curing studies were carried out with the sulfonyl aziridines and Butarez and Telagen polymers at 200°F to see if we could obtain products for thermal aging studies. The trifunctional sulfonyl aziridine (XVII) reacted with the Butarez carboxy polymer to give a clear, non-tacky, hard, brittle product within 24 hours even though there was poor dispersion of the curative. At 150°F the product was tacky and rubbery after 6 days.



XVII



XVIII

A 50/50 equivalent mixture of the tri- and difunctional (XVIII) curatives gave a product with Butarez that was brittle after 65 hours at 200°F while the difunctional curative gave a product that was extremely tacky.

With the saturated Telagen polymer the trifunctional curative showed no cure after 10 days at 150°F, and at 200°F the product was a tacky solid after 4 days. In the presence of a BF_3-tributyl phosphate catalyst the system showed signs of curing after 18 hours but only reached a gel state. This low state of cure was due to the very poor dispersion of the sulfonyl aziridine in the polymer.

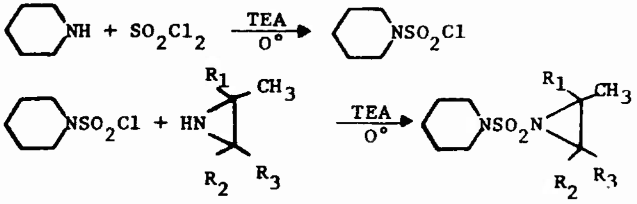
To get satisfactory cures with the sulfonyl aziridine system, we need a good catalyst. Catalyst studies have continued with model compounds to find catalysts that will increase the rate of reaction between sulfonyl aziridines and carboxylic acids. Several of the results appear promising, but so far a satisfactory catalyst has not been found.

B. ATTEMPTED SYNTHESIS OF MODEL N-SULFAMOYL AZIRIDINES

An attempt was made to synthesize several N-sulfamoyl aziridines by the sequence

I

II



Ia. $R_1=CH_3, R_2, R_3=H$

Ib. $R_1, R_2=H, R_3=CH_3$

Piperidinyl-N-sulfonyl chloride was made (Equation I) satisfactorily and isolated as a liquid (1).

No product was isolated when piperadine-N-sulfonyl chloride and either 2,2-dimethyl aziridine or <u>cis</u>-2,3-dimethyl aziridine were mixed with triethylamine (TEA) catalyst in ether solution.

It is possible that the reaction between piperidine-N-sulfonyl chloride and 2,2-dimethyl aziridine or <u>cis</u>-2,3-dimethyl aziridine requires a higher temperature or longer reaction time. Hall (1) reports that hydrolysis or nucleophilic attack on N,N-dialkyl sulfamoyl chlorides are slow compared to attack on alkyl sulfonyl chlorides.

No other attempt to prepare the above compounds will be made.

C. SYNTHESIS AND EVALUATION OF N-ACYL AZIRIDINES

The 2,3-dimethyl N-acyl aziridine system is being examined as an approach to increasing the cure rate and miscibility while retaining the selectivity and storage stability of the sulfonyl aziridines. The 2,3-dimethyl acyl aziridines should have better selectivity for the acid addition reaction and better storage stability than HX-868, the 2-ethyl aziridine derivative of trimesic acid. At the same time they should have faster rates and better miscibility in the polymers than the sulfonyl aziridines.

In model compound studies the <u>cis</u>-2,3-dimethyl acyl aziridine had a much faster rate of reaction than the sulfonyl aziridine, and as expected, a slower rate than HX-868. In the reaction with octanoic acid in toluene at 150°F the trifunctional <u>cis</u>-2,3-dimethyl acyl aziridine had a half-life of about 8 days <u>vs</u> a half-life of 58 hours for HX-868. Satisfactory gumstock cures have been made with the trifunctional dimethyl acyl aziridine and with combinations of tri- and difunctional dimethyl acyl aziridines.

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(1) H. K. Hall, Jr., J. Am. Chem. Soc., <u>78</u>, 1450 (1956).

1. Evaluation of Commercially Available Di- and Trifunctional N-Acyl Aziridines

Commercially available N-acyl aziridines which have been used as curatives were examined to determine their reaction rates and selectivity with model carboxylic acids. The performance of these aziridines is used throughout our work as standards to evaluate the rate and selectivity of new aziridines. The 2-ethyl aziridine derivative of trimesic acid (HX-868 from 3M) is used in several binder systems so its performance is used as the primary standard in most of our evaluations. This aziridine has been reported to contain polymeric fractions , and is known to undergo rearrangement to an oxazoline structure. The oxazoline has a much lower rate of reactivity with carboxyl groups than the aziridine ring. The development of HX-868 as a propellant curative, and its use as a replacement for MAPO, was particularly related to the improved propellant hydrolytic stability achieved with this aziridine.

The aliphatic acyl aziridines reacted rapidly with octanoic acid and had fairly good selectivity. The aromatic acyl aziridines were slower and had poorer selectivity. In the reaction of HX-868 with octanoic acid about 30% of the acid is unreacted after the aziridine has disappeared. A large portion of the aziridine appears to undergo rearrangement to the oxazoline. The reaction of HX-868 with excess acetic acid at room temperature is extremely fast with the reaction having a half-life of slightly more than two minutes.

Gumstock studies have been made with HX-868 and Butarez CTL Type II prepolymer. Gumstocks cured at 150°F for four days had fairly good initial modulus values, but relatively low stress and strain properties.

Baseline gumstock rings have been prepared from a new lot of Telagen CT cured with HX-868, for determination of tensile properties before and after aging. Preliminary aging of Telagen CT/HX-868 gumstock rings under N_2 at 275°F for seven days was accompanied by severe degradation of tensile properties. Stress relaxation modulus and crosslink density of gumstock made in the presence of AP were lower than those of gumstock made without AP.

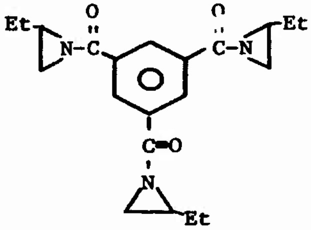
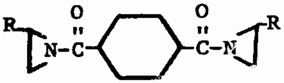
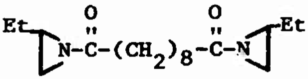
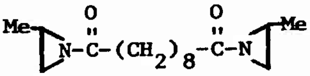
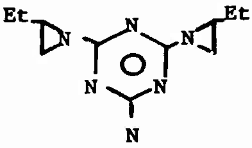
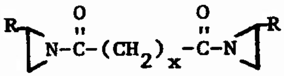
1.1. Model Carboxylic Acid Studies

The reaction rate of HX-868 with excess acetic acid was obtained at room temperature. The rate was quite rapid, as shown in Figure 17, with the reaction having a half-life of about 2 minutes 20 seconds. This is considerably faster than the corresponding reaction for sulfonyl aziridines where the 2-phenyl sulfonyl aziridine had a half-life of 6 hours at 25°F and the 2-methyl sulfonyl aziridine had a half-life of about 30 hours at 50°C.

Several commercially available N-acyl aziridines were reacted with octanoic acid in dichlorobenzene to determine their reaction rates and selectivity for the acid addition reaction. The six commercial aziridines shown in Table XXIV were reacted with an equivalent amount of octanoic acid in O-dichlorobenzene at 150°F. Reactions were followed by infrared measurements until no changes were observed. The reaction time and the acid remaining at the end of the reaction are listed.

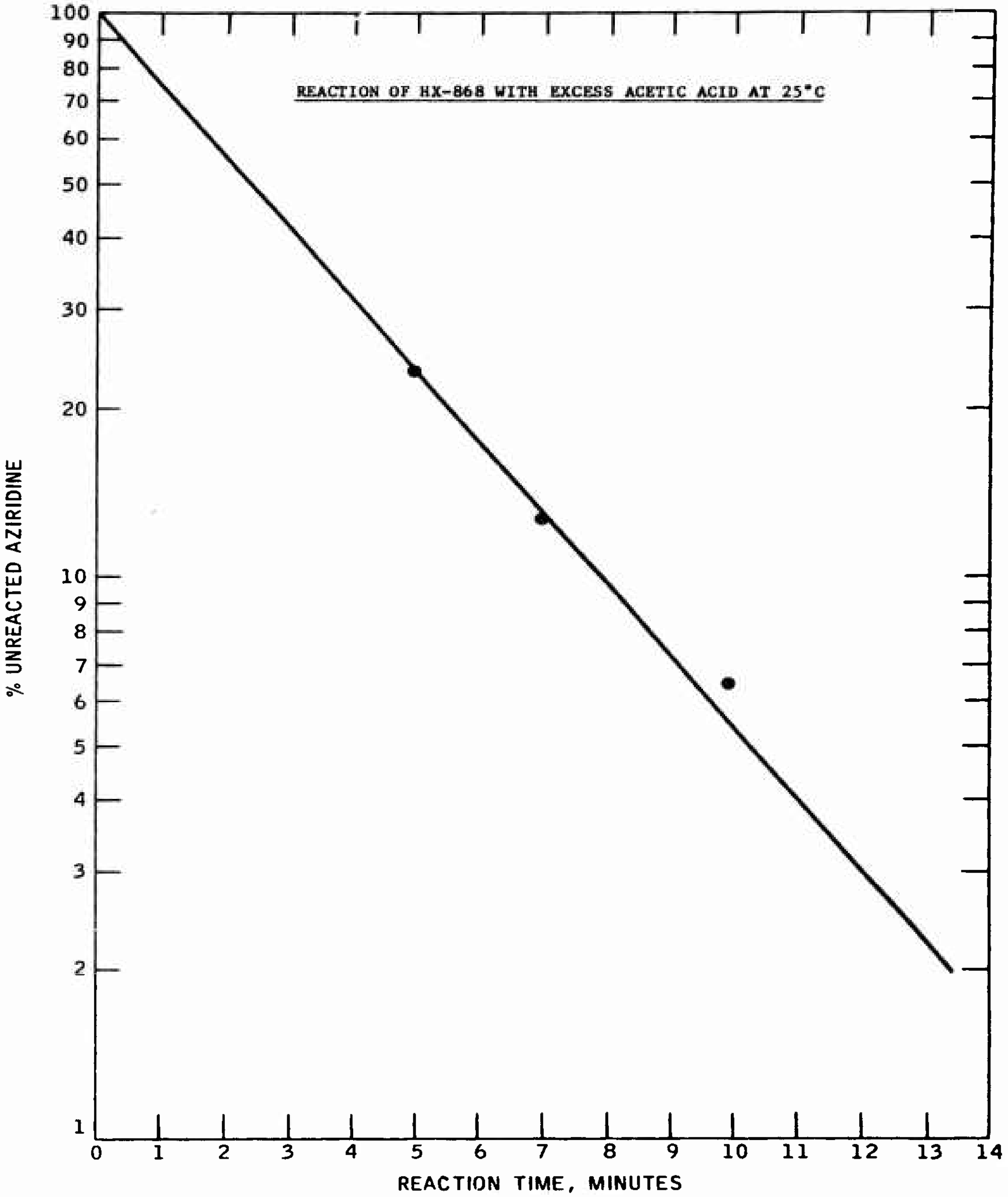
TABLE XXIV

REACTION OF 3M AZIRIDINES WITH OCTANOIC ACID(1)

Trade Ident.	Aziridine Structure	IR Abs. μ	Time to Complete Reaction, Hrs.	Acid Recovery,%
HX 868		8.35	22	26.1
HX 752		8.35	21	21.2
HX 760		10.7	2	15.5
HX 740		10.7	2	13.9
HX 874		10.7 12.0	2	13.4
HX 753		11.0	1.3	6.8

(1) Aziridine/Acid = 1:1; 20% in dichlorobenzene; 150°F

FIGURE 17


REACTION OF HX-868 WITH EXCESS ACETIC ACID AT 25°C
% UNREACTED AZIRIDINE
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
REACTION TIME, MINUTES

The aliphatic acyl aziridines were extremely fast with good selectivity towards acid (6.8-15.5% acid remaining). The aryl acyl aziridines were decidely slower with poor selectivity (21.2-26.1% acid remaining).

The reaction of HX-868 with octanoic acid was also studied at 10% concentration in toluene at 120°F and 150°F and neat at 120°F. In the absence of solvent the reaction was completed within 14 hours based on the disappearance of aziridine. However, there was still 20% unreacted acid indicating that substantial side reaction had occurred. Figure 18 shows the reaction profile for the reaction of HX-868 with octanoic acid in toluene at 120°F. This reaction was followed by the disappearance of aziridines in the infrared.

The initial reaction is very rapid with 25% of the aziridine reacting in about 3 hours. The reaction tapers off appreciably after that and the half-life is about 20 hours. When the reaction was completed there was still 34% acid remaining.

Figure 19 shows the reaction of HX-868 with octanoic acid in toluene at 150°F. The rate of reaction in this case was followed by the disappearance of octanoic acid by titration with tetrabutyl ammonium hydroxide. This curve shows that the addition reaction is quite a bit slower than would be predicted from following the disappearance of aziridine. The half-life of this reaction is about 58 hours vs the 20 hour half-life for the disappearance of aziridine at 120°F. The acid reaction curve also shows that 30% of the acid is still remaining at the end of the reaction. HX-868 appears to have a good rate of reaction but has poor selectivity for the addition reaction.

HX-868 was also reacted with octanoic acid in toluene at 150°F in the presence of ammonium perchlorate. AP was added to the reaction mixture at a level of 5% based on the total solution. The reaction was monitored by titrating for octanoic acid with tetrabutyl ammonium hydroxide. The results are listed in Table XXV.

TABLE XXV

REACTION OF HX-868 WITH OCTANOIC ACID IN TOLUENE AT 150°F IN THE PRESENCE OF AMMONIUM PERCHLORATE(1)

	% Unreacted Acid	
Reaction Time	No AP Present	AP Present
19 hours	69.7	68.4
28 hours	63.8	63.5
48 hours	53.0	52.4
96 hours	40.0	39.0

---

(1) 10% concentration of acid and aziridine; 5% AP based on total solution.

The AP appears to have no effect on the rate of reaction.

FIGURE 18

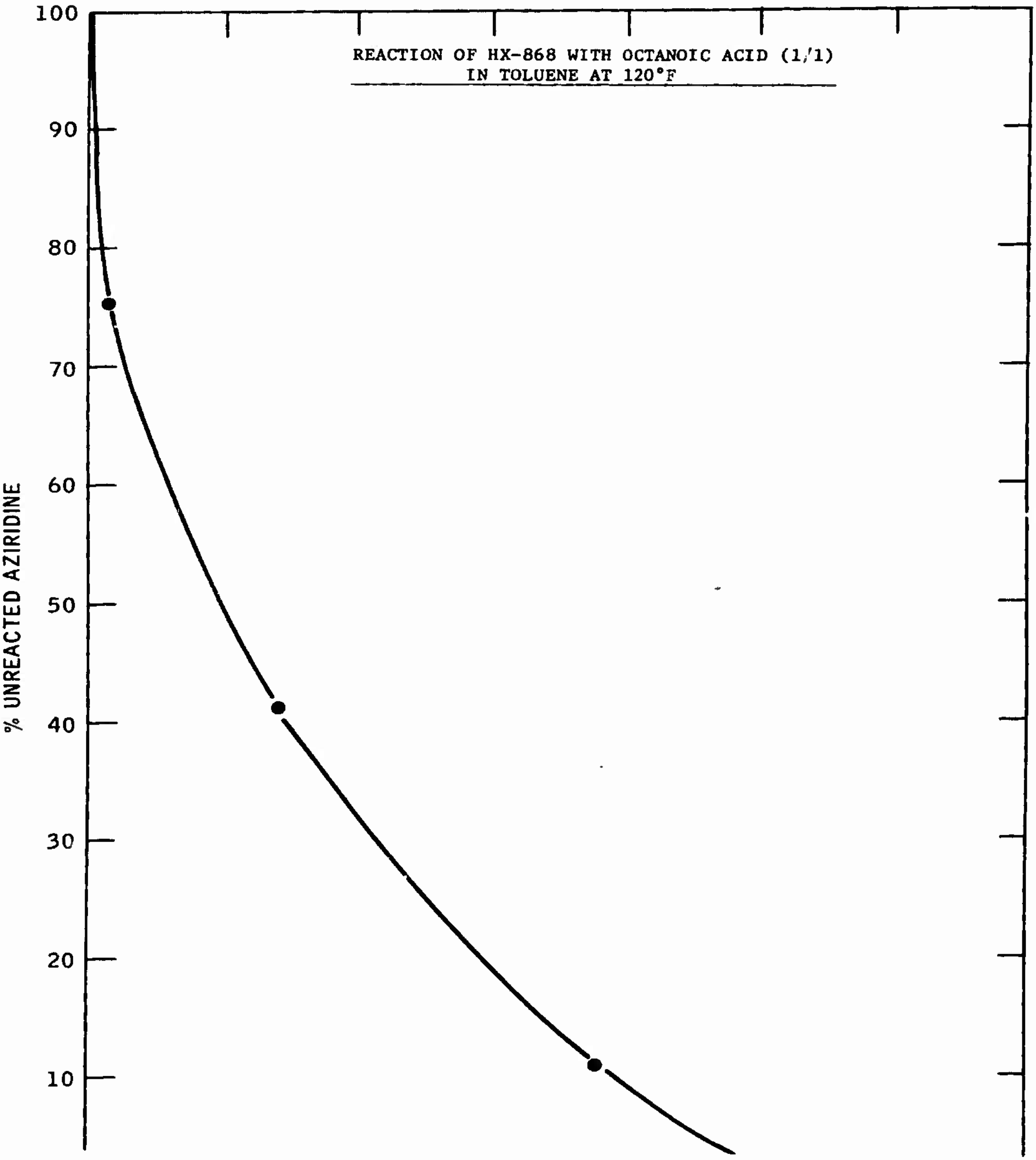
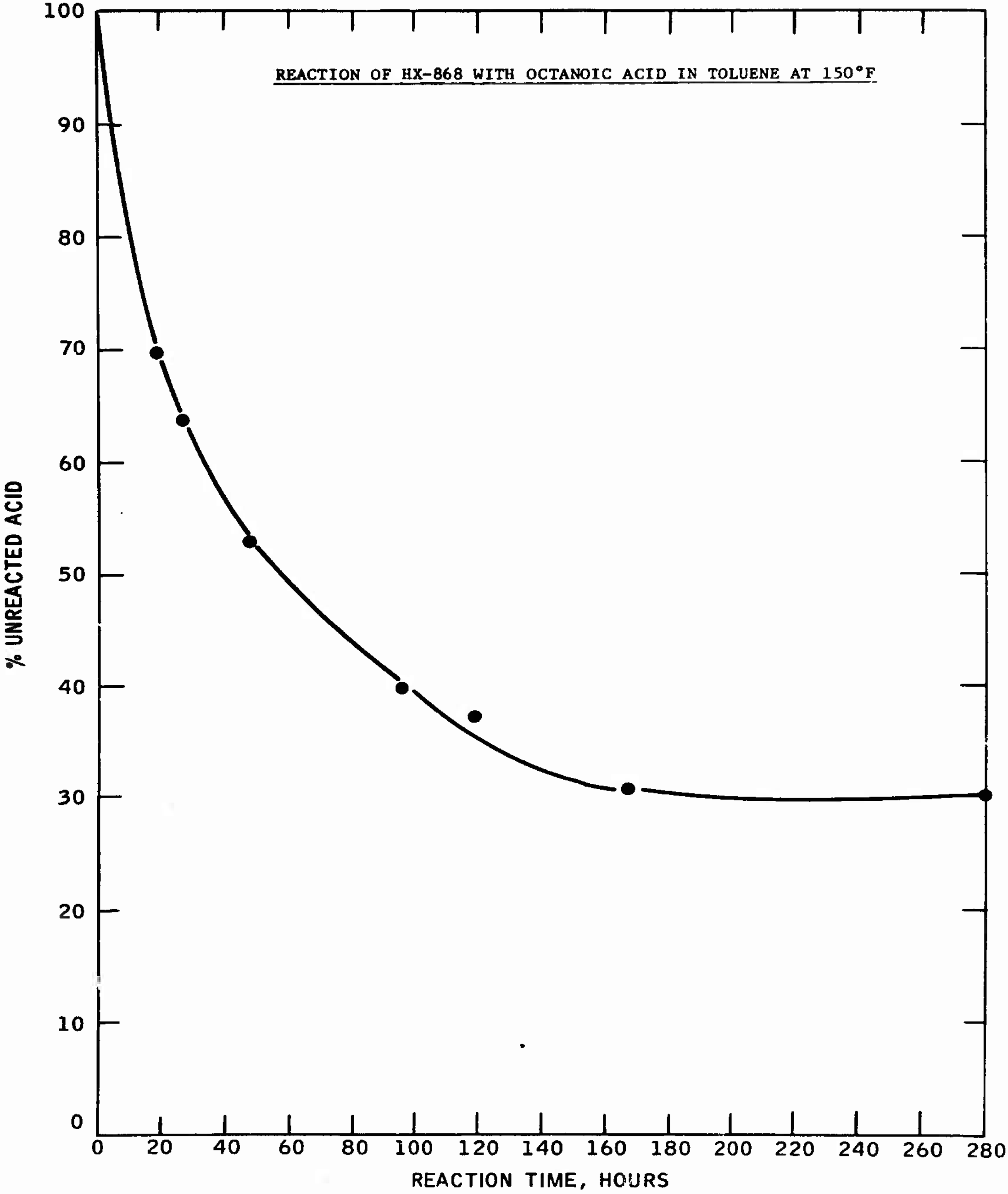

REACTION OF HX-868 WITH OCTANOIC ACID (1/1) IN TOLUENE AT 120°F
100
90
80
70
60
50
40
30
20
10
% UNREACTED AZIRIDINE

FIGURE 19


REACTION OF HX-868 WITH OCTANOIC ACID IN TOLUENE AT 150°F
% UNREACTED ACID
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
REACTION TIME, HOURS

1.2. Evaluation of HX-868 with Butarez Type II CTPB

Gumstock studies were made with Butarez CTL Type II prepolymer cured with HX-868 to establish comparative reference points for the new curing systems Gumstocks were prepared by mixing the prepolymer and the curative on a micromill and curing in molds. Micro dumbbells were cut from the cured pads and mechanical properties were measured on the dumbbells. Thermal aging studies were carried out on pads, from which dumbbells were cut for testing. Mechanical properties were measured at ambient temperature at a strain rate of 2 inches/minute. A minimum of three samples was used for testing mechanical properties.

In the initial studies samples were prepared at a stoichiometric ratio of carboxy/aziridine and were cured at 120°F for 3 to 17 days and at 150°F for 2 to 5 days. The equivalent weight values used for HX-868 were determined by titration in our laboratory (134 determined <u>vs</u> 142 reported by 3M Company <u>vs</u> 123 theoretical). The mechanical properties of the cured samples at ambient temperature are listed in Table XXVI.

TABLE XXVI

MECHANICAL PROPERTIES OF BUTAREZ CTL GUMSTOCKS AT AMBIENT TEMPERATURE CURED WITH HX-868

Cure		Hardness	Maximum	
Temp. °F	Time, Days	Shore A	Stress, psi	Strain, %
120	3	35	95	240
120	4	35	95	240
120	7	37	95	170
120	17	38	110	180
150	2	38	80	210
150	5	51	90	170

The system appears to reach maximum elongation within 3 days at 120°F, but does not appear to be completely cured in 2 days at 150°F. There also appears to be some thermal aging effects after 17 days at 120°F and after 5 days at 150°F.

Thermal aging effects on this system were examined at 180°F and 275°F in a nitrogen atmosphere. Samples were aged at 275°F for up to 7 days and at 180°F for up to 2 weeks. The results of these aging studies are given in Table XXVII.

TABLE XXVII

THERMAL AGING OF BUTAREZ CTL GUMSTOCKS CURED WITH HX-868[1]

	Hardness, Shore A	Max. Stress, psi	Strain, %	Initial Modulus, psi
Days Aged @ 275°F In Nitrogen Atmosphere				
0	51	90	170	80
1	61	120	160	120
4	47	100	160	90
7	48	90	80	150
Days Aged @ 180°F In Nitrogen Atmosphere				
0	51	90	170	80
7	47	100	120	110
14	51	110	130	100

---

(1) Cured 5 days at 150°; Aziridine/COOH=1; Results are an average of three samples.

After 1 day at 275°F there appears to be additional crosslinking as evidenced by the greater hardness and higher tensile. After 4 days there is slight degradation and after 7 days there is significant degradation in strain.

While the effect on hardness and stress does not seem to be as great at 180°F there is a significant reduction in strain at 7 days at 180°F.

Another gumstock study was made using the reported value of 142 for the equivalent weight of HX-868. This sample was cured for 4 days at 150°F and was aged at 275°F for up to 14 days. The mechanical properties of these samples are listed in Table XXVII.

TABLE XXVIII

THERMAL AGING OF BUTAREZ CTL TYPE II GUMSTOCKS CURED WITH HX-868(1)

Days Aged @ 275°F In Nitrogen Atmosphere	Hardness Shore A	Max. Stress psi	Strain, %	Initial Modulus psi
0	35	70	200	60
4	48	90	130	130
7	42	90	120	130
14	40	100	120	130

---

(1) Cured 4 days at 150°F; Aziridine/COOH=1;
Average of 3 samples.

After 4 days at 275°F there is significant degradation in the strain values, while the modulus shows a significant increase. Both of these changes are undesirable for good binder properties.

1.3. Evaluation of HX-868 with Telagen CT (Base Case)

The baseline gumstock for these studies is Telagen CT cured with the trifunctional aziridine HX-868 at 1.0/1.0 amine to carboxyl ratio.

Gumstock was prepared from COOH prepolymers and HX-868 by vacuum mixing, and curing slabs in ASTM molds. From the cured slabs, rings having inside diameter of 1.0 inch and cross section of 0.0052 in^2 were cut. Prior to receipt of the standard prepolymers from General Tire and Rubber Co., a preliminary study was performed to evaluate the ring preparation and testing techniques. Both Butarez CTL and Telagen CT lots available at LPC were employed.

The presence of AP reportedly influences the cure rate and curative side reactions. To evaluate the effect that AP has on cured gumstock properties, one of the Telagen gumstocks was mixed in the presence of AP. Only a small fraction of AP dissolved. The Butarez gumstock was adequately cured in 5 days at 160°F, while the Telagen gumstocks were soft after 5 days cure at 140°F (Shore A hardness 17). They were therefore wrapped in aluminum foil and cured an additional two weeks at 165°F, after which the Shore A hardness had increased to 45-50. Mechanical properties measured on ring specimens are compared in Table XXIX.

TABLE XXIX

MECHANICAL PROPERTIES OF GUMSTOCK RINGS AT 70°F

	Temp. °F	Cure Time, Days	Stress psi	Strain Percent
Butarez CTL/HX-868 (1.0/0.95)	160	5	98	145
Telagen CT/HX-868 (1.0/1.0)	140	5		
	165	14	79	79
Telagen CT/HX-868 (1.0/1.0),	140	5		
(AP saturated)	165	14	56	124

The Butarez gumstock rings showed higher stress and strain than the Telagen CT gumstock, even though the latter had been subjected to much more cure. This reflects the varying functionality of the two prepolymers. Tensile data as a function of temperature for the Telagen gumstock are presented in Figures 20 and 21. The gumstock made in the presence of AP shows higher strain at temperatures above 20°F, and somewhat lower stress at all temperatures between -75° and 160°F. These data will serve as reference for subsequent evaluation of the relative sensitivities of new curatives to AP.

1.3.a. Stress Relaxation and Crosslink Density of "Unaged" Gumstock

Preliminary testing was performed on the same Telagen CT/HX-868 gumstock described in Section 1.3., made in the presence and absence of AP. The test objectives were to determine the effect of load rate and strain level on stress relaxation modulus in these two systems, and to calculate effective crosslink density from such data.

The stress relaxation data are plotted in Figures 22 and 23. The gumstock made in the presence of AP showed a lower modulus and a lower fail time at high strain levels; this parallels the previously observed 70 percent failure strain (90°F) of gumstock without AP versus a value of 125 percent for one with AP (Figures 20 and 21).

Calculation of the effective crosslink density was undertaken from the following equation:

$$\rho = (Ve/V)\ RT\ [1 + \epsilon - \frac{1}{(1 + \epsilon)^2}]$$

where: ρ/ϵ = equilibrium modulus ($\rho = \frac{F}{A_o}$, ϵ = strain)

(Ve/V) = moles of effective crosslinks/unit volume

Computed effective crosslink densities based on the longest relaxation time modulus tested (20 minutes) are presented in Table XXX. It is apparent that the calculated values do not vary strongly with strain above 16 percent or with rate of extension. The effect of dissolved AP, however, is quite pronounced.

FIGURE 20

STRESS-STRAIN DATA OF TELAGEN CT/HX-868 GUMSTOCK CURED FOR 5 DAYS AT 140°F AND 2 WEEKS AT 165°F AS A FUNCTION OF TEST TEMPERATURE

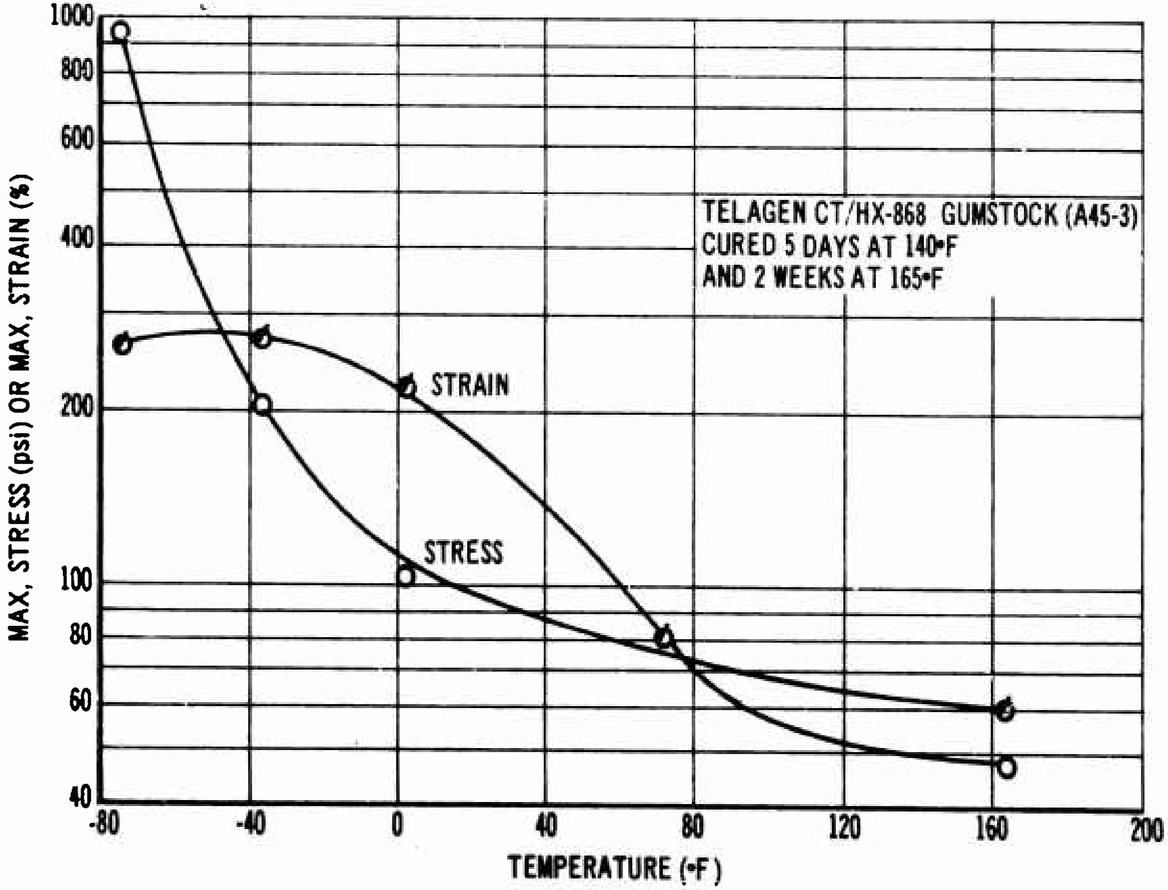


FIGURE 21

STRESS-STRAIN DATA OF TELAGEN CT/HX-868 GUMSTOCK CURED IN THE PRESENCE OF AP AS A FUNCTION OF TEST TEMPERATURE

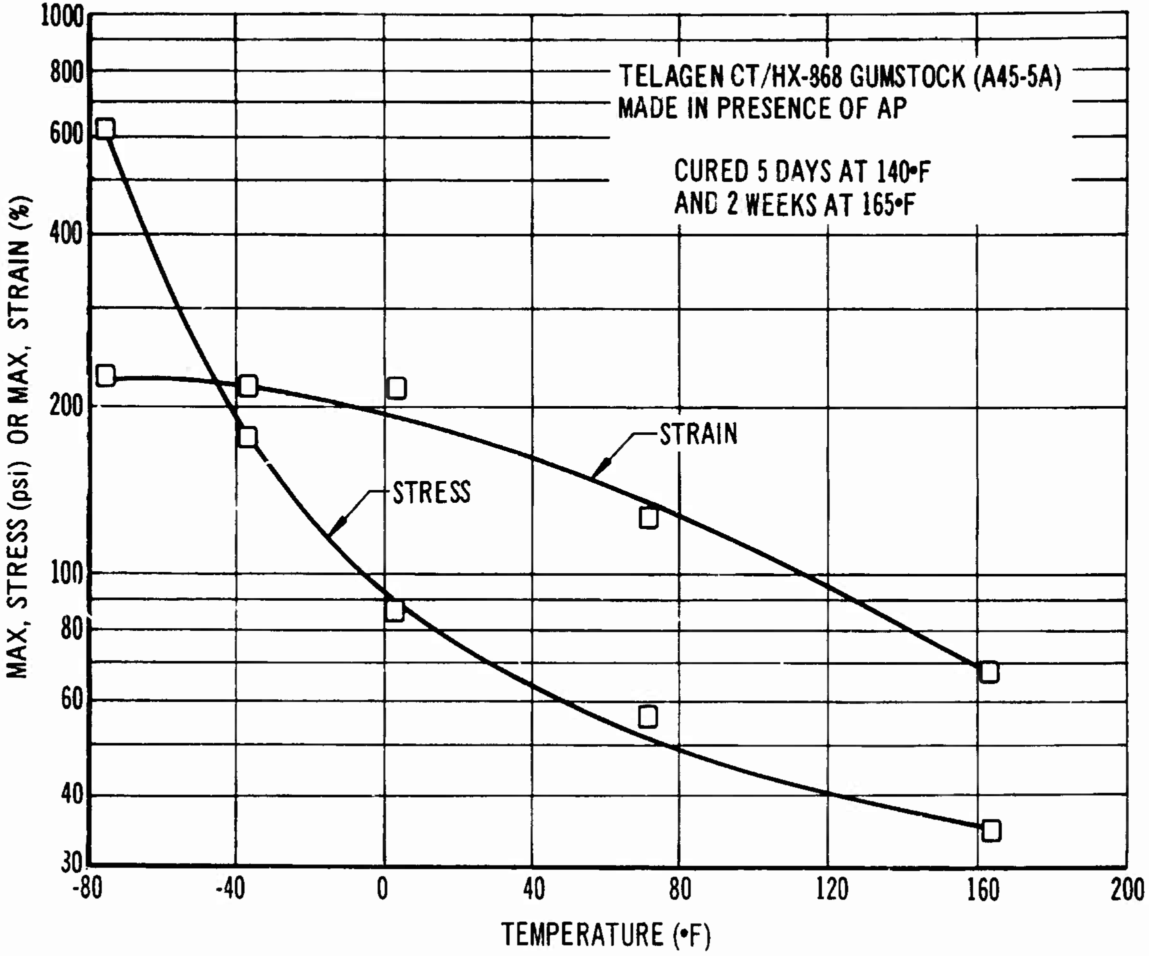


FIGURE 22

STRESS RELAXATION DATA FOR TELAGEN CT/HX-868 CURED IN THE PRESENCE AND ABSENCE OF AP

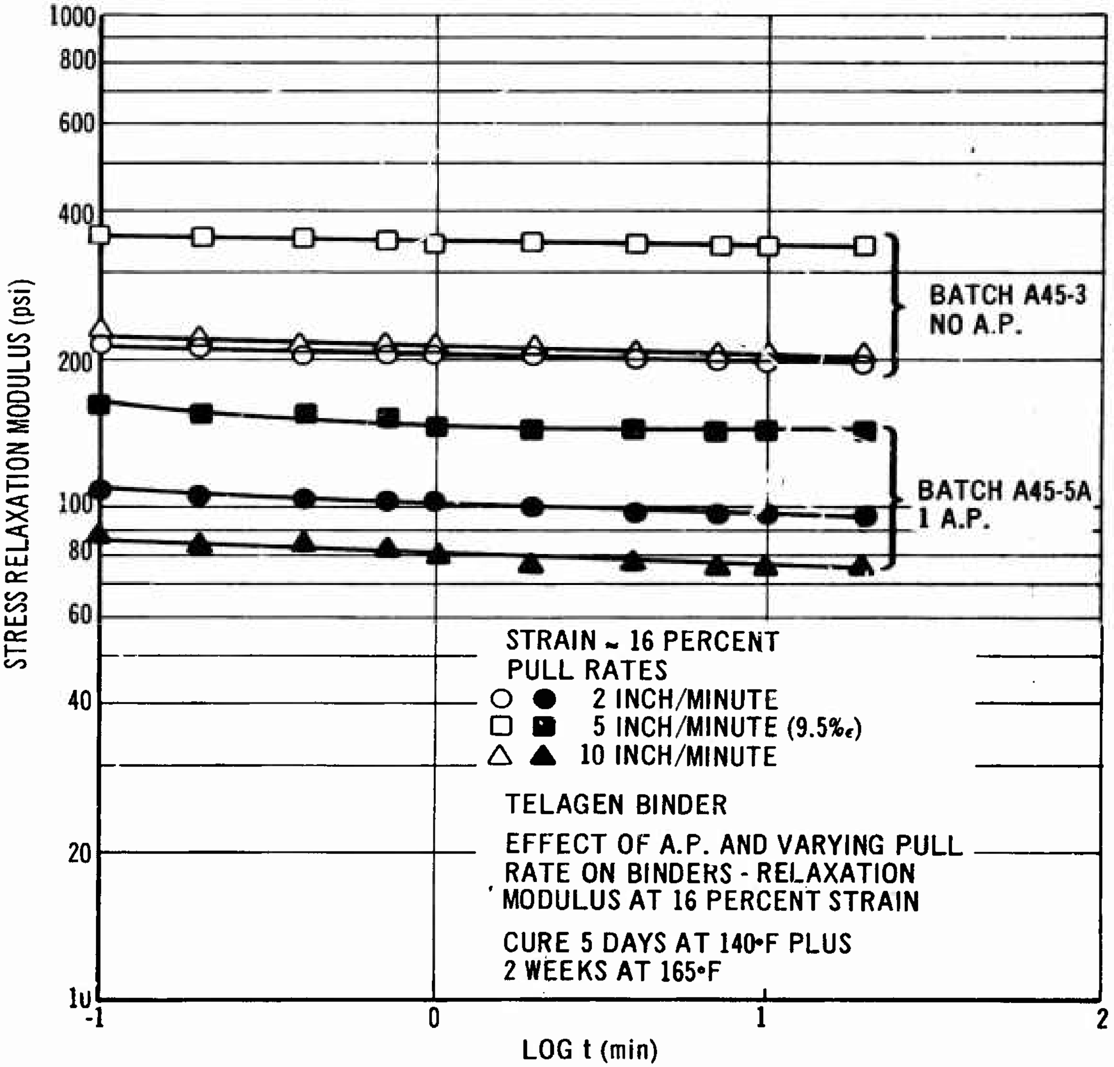


FIGURE 23

EFFECT OF AP AND VARYING PULL RATE ON RELAXATION MODULUS AT 50% STRAIN

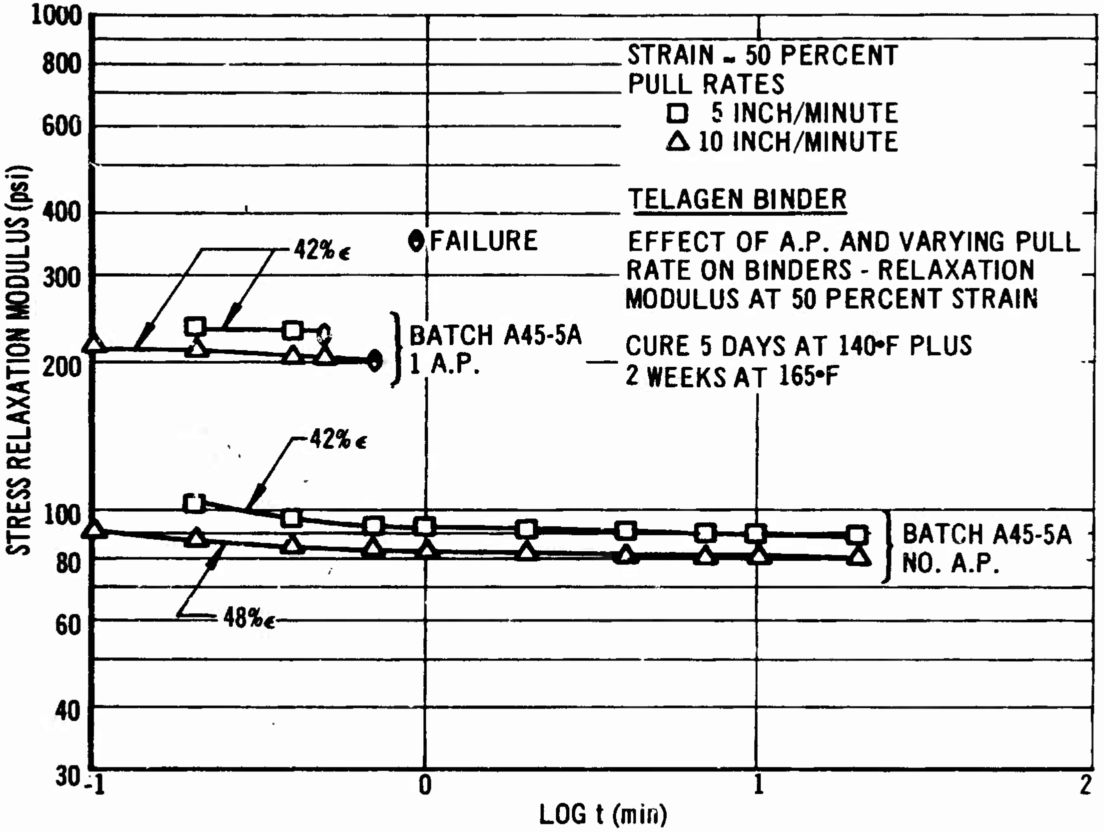


TABLE XXX

CROSS LINK DENSITY FOR COOH TELAGEN, HX-868 GUMSTOCK(a)

COOH Telagen, HX-868 Gumstock	Strain %	Rate Min^{-1}	X-Link Density (moles/cm^3) x 10^{-5}	
No AP	9.57	5	6.85	
AP	9.57	5	2.92	
No AP	16.1	10	4.26	4.18 average
		2	4.10	
AP	16.1	2	2.00	1.80 average
		10	1.59	
No AP	41.6	5	4.20	4.15 average
	42.0	10	4.10	
AP	41.7	5	1.81	1.62 average
	48.4	10	1.43	

(a) Imine/carboxyl ratio 1.0/1.0. Cured 5 days at 140°F and two weeks at 165°F.

1.3.b. Aging of Gumstock at 275°F

Preliminary aging was carried out in N_2 at 275°F on gumstock rings prepared from Telagen CT/HX-868 in the absence of AP. The rings were wrapped in aluminum foil and canned in N_2 before aging. After 7 days at 275°F the rings were brittle, and showed 0 percent strain. A bulk specimen of gumstock (0.7 cm thick) aged at 250°F in N_2 for seven days did not become brittle, although the surfaces darkened to a depth of 0.2 cm. After aging, Shore A hardness (surface) was 35 compared to original value of 20. Based on these data, high temperature aging of the Telagen CT/HX-868 gumstock will be carried out at 250°F rather than 275°F.

1.3.c. Telagen CT/HX-868 Gumstock for Tensile Testing and Aging

When the base lot of Telagen CT (Lot 242 AM 273 CR) arrived, a three-pound quantity of the Telagen CT/HX-868 gumstock was prepared by vacuum treating the prepolymer at 90°F for 40 minutes, then incorporating the curative. Particles of undissolved HX-868 were present after 20 minutes mixing at 85-90°F. Complete solution of the curative was accomplished by raising the temperature to 120°F and mixing an additional 20 minutes. Bulk gumstock cure was followed by measuring viscosity with a Brookfield Viscometer. The data, summarized in Table XXXI, will be correlated with analytical studies of the cure process to be conducted shortly.

TABLE XXXI

VISCOSITY OF TELAGEN CT/HX-868 GUMSTOCK

(Brookfield Viscometer, Spindle No. 2)

Hours after Mixing	Viscosity Cps at 140°
1	2800(1)
3	9600
6	48,000
22	Polymerized

---

(1) Telagen CT (lot 242 AM 273 CR) has a viscosity of 800 cps at 140°F

Slabs of gumstock (0.075" thick) were prepared in ASTM molds, using a five day cure at 140°F. The slabs were slightly tacky, with Shore A hardness of 20. Ring specimens were cut from these slabs for testing and aging, since five day cure at 140°F is representative of propellant cure. The aging program will continue for eight weeks.

2. Synthesis and Evaluation of Monofunctional N-Acyl Aziridine

N-Acyl derivatives of cis- and trans-2,3-dimethyl aziridine, and 2-methyl aziridine were synthesized by reacting at 0° the acyl chlorides with the appropriate aziridine in the presence of equimolar quantities of triethylamine. Ethyl ether was used as the reaction solvent. Physical properties, yields, and aziridine analysis are listed in Table XXXII. Satisfactory analytical data were obtained for each compound. Infrared spectra are found in Appendix C3.

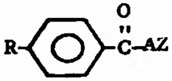
No oxazolines were found as impurities. This was determined by comparing several purified N-acyl aziridines with their corresponding oxazolines. Chemical shifts of the methyl groups in 3 membered aziridine rings were different from the methyl groups in the 5-membered oxazoline ring.

The yields of N-acyl aziridines were moderate, ca. 50-60%, and may reflect losses due to copious water washes of the reaction solution. This was done to insure complete removal of triethylamine hydrochloride which can act as a catalyst for ring opening or rearrangement reactions.

On one N-acyl aziridine a titration using the acetic acid-hydrobromic acid technique was done. The experimental value found agreed well with calculated.

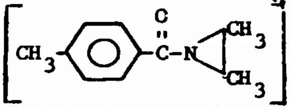
TABLE XXXII

N-ACYL AZIRIDINES



R	AZ	M.P. °C	Yield, %	Meq. AZ N/g Sample Actual	Meq. AZ N/g Sample Found
NO_2	2-MeAZ	78.5-79	61	(a)	(a)
NO_2	cis-2,3-diMEAz	146-146.5	54	(a)	(a)
CH_3	cis-2,3-diMEAZ	48-51	68	5.29	5.24
NO_2	trans-2,3-diMEAZ	(a)	(a)	(a)	(a)

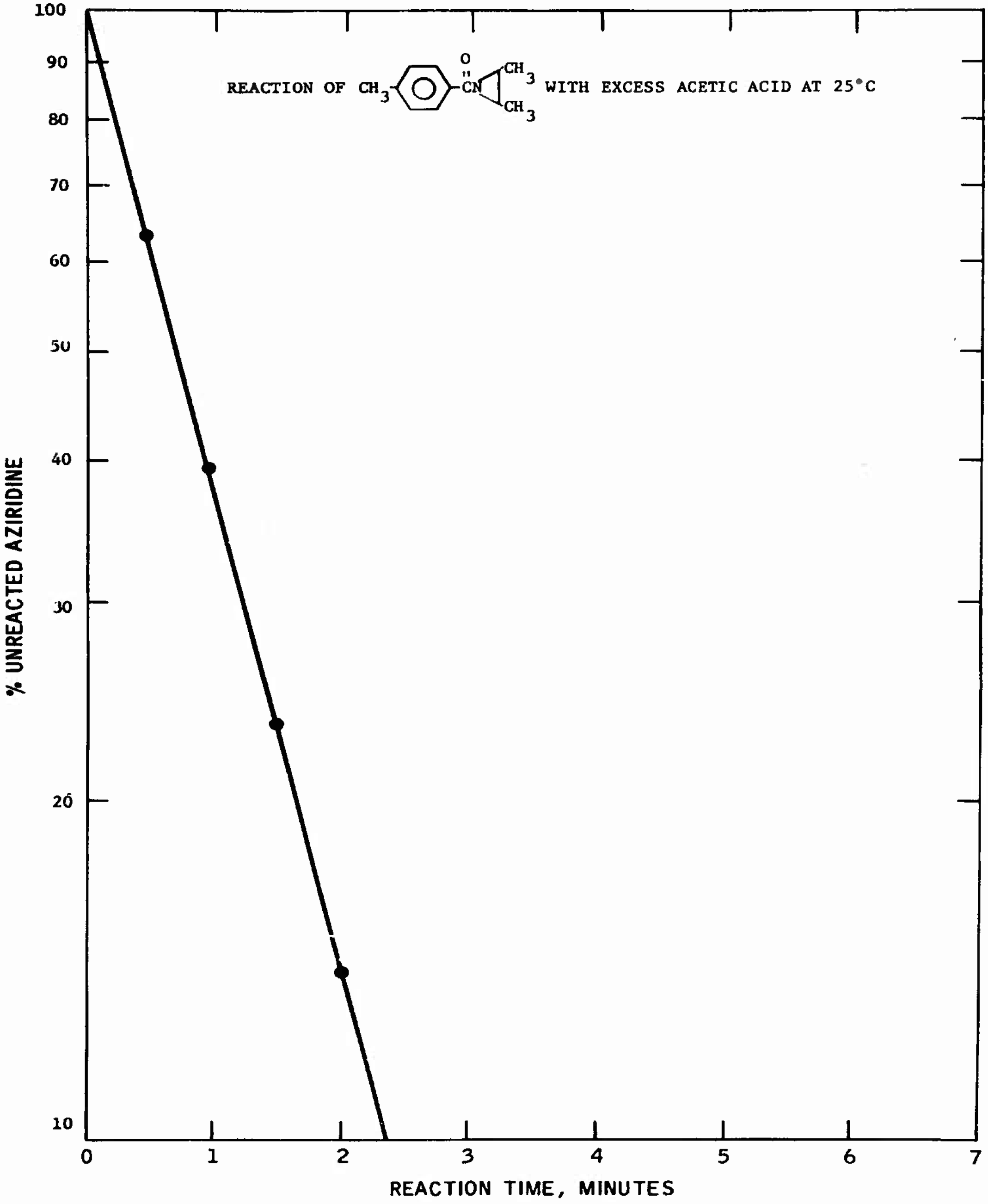
(a) Not determined

Preliminary evaluation of the 2,3-dimethyl acyl compounds was carried out with N-(p-methylbenzoyl)-cis-2,3-dimethyl aziridine  and octanoic acid. This compound reacts much slower with octanoic acid than the monosubstituted acyl aziridines which were discussed in 1.1 above.

After 22 days at 120°F in a toluene solution, there was still 37.3% unreacted aziridine according to the infrared spectra calculations. At the same time the acid titration showed 36.3% unreacted acid, which indicates excellent selectivity in the reaction. In a separate experiment the 2,3-dimethyl acyl aziridine was reacted with BF_3·etherate (10% based on aziridine) in toluene. After 8 days there was no disappearance of aziridine according to the infrared spectra which indicates that side reactions may not be a serious problem with these materials.

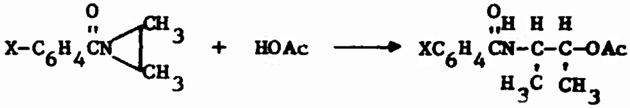
The reaction rate of N-(p-methylbenzoyl)-cis-2,3-dimethyl aziridine with excess acetic acid was obtained at room temperature. The reaction was extremely rapid as shown in Figure 24, with a half-life of 40-45 seconds. This indicates that the reaction of the cis-2,3-dimethyl derivative is faster than for HX-868. While this may be true for the monofunctional material in the acetic acid system it is not confirmed by the reaction of the trifunctional counterpart with octanoic acid in toluene which is described below.

FIGURE 24


REACTION OF CH3-C6H4-C(=O)N(CH-CH3)(CH-CH3) WITH EXCESS ACETIC ACID AT 25°C
% UNREACTED AZIRIDINE
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
REACTION TIME, MINUTES

The reaction of p-nitrobenzoyl cis-2,3-dimethyl aziridine and p-toluoyl cis-2,3-dimethyl aziridine with excess acetic acid lead to the esters according to Equation 1.

(1)



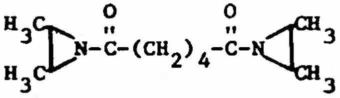
X = NO_2, CH_3

Only the threo isomers were formed as determined by the NMR spectra. Under these conditions the reaction was almost quantitative, no ring expansion to oxazolines and little or no polymerization occurred.

3. Synthesis of Di- and Trifunctional cis-2,3-Dimethyl-N-Acyl Aziridines

3.1. Synthesis of Difunctional Aliphatic Acyl Aziridine

A difunctional aliphatic-acyl aziridine was synthesized from freshly distilled adipoyl chloride and cis-2,3-dimethylaziridine. Although 63 g. was expected only 5.0 g. of material was isolated (8% yield). The IR, NMR and elemental analysis analyzed for I. A small amount of carboxylic acid was detected by titration and IR analysis.



(I)

Another attempt was made to synthesize this material, but on a smaller scale to determine where product was lost.

A longer reaction time and excess aziridine were used. The reaction was worked up after it was determined by IR that all acyl chloride had reacted. A crude yield of 36% was obtained which was reduced to 24% after purification, m.p. 56-57°C. The IR is shown in Appendix C3.

The low yields may be due to the curatives solubility in the large amount of water which is used during workup. This will be checked out when and if we have to make larger batches for gumstock evaluations.

3.2. Synthesis of a Trifunctional Aromatic Acyl Aziridine

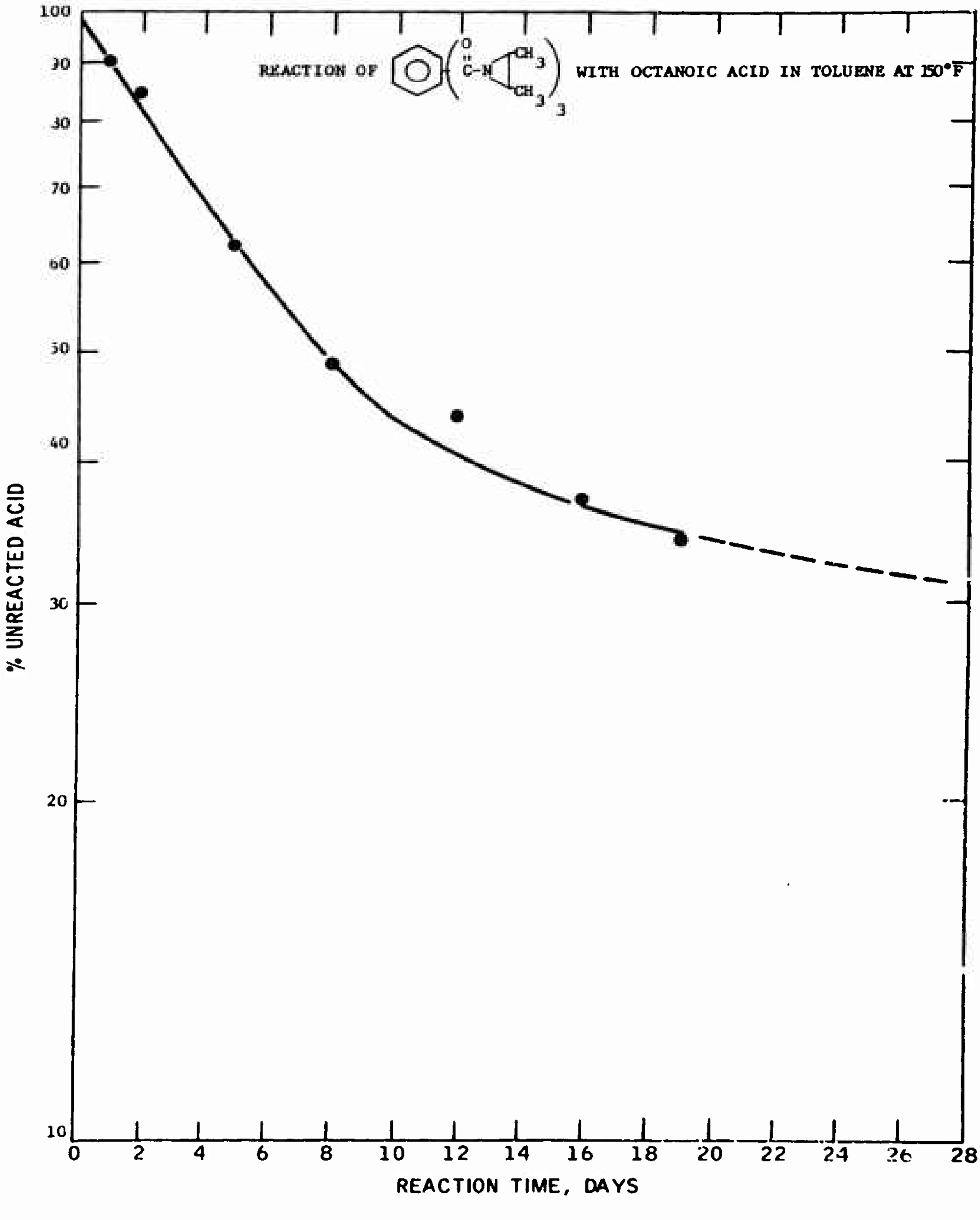
The first attempt to make the tris-cis-2,3-dimethylaziridine of trimesic acid resulted in a low yield (~35%) with questionable purity (a small carboxyl OH detected by IR). A repeat of this reaction with longer reaction times (24 hrs) and a slight excess of aziridine gave an improved product. The yield was still low however (~53% recrystallized) m.p. 161-162.5°C. The IR is shown in Appendix C3. This material is being used for our preliminary cure studies.

4. Evaluation of Di- and Trifunctional cis-2,3-Dimethyl-N-Acyl Aziridines

4.1. Model Carboxylic Acid Study

The reaction of the trifunctional cis-2,3-dimethyl acyl aziridine with octanoic acid was examined at 150°F, at a 10% concentration in toluene. The reaction was followed by the disappearance of octanoic acid by titration with tetrabutylammonium hydroxide. The curve in Figure 25 shows that the rate is considerably slower than the rate for the corresponding reaction with HX-868 (Figure 19.

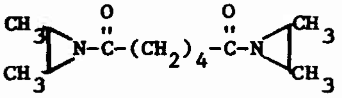
FIGURE 25


REACTION OF
O
C-N
CH3
CH3
3
WITH OCTANOIC ACID IN TOLUENE AT 150°F
100
90
80
70
60
50
40
30
20
10
% UNREACTED ACID
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
REACTION TIME, DAYS

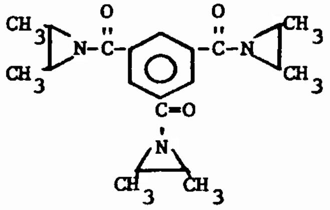
The half-life for the cis-2,3-dimethyl aziridine derivative is about 8 days vs a half-life of 58 hours for the HX-868 reaction. This indicates that the trans-2,3-dimethyl acyl aziridine derivative should be examined if a faster cure rate is needed. However, this can be determined only from gumstock and propellant studies.

4.2. Gumstock Studies with Butarez Type II CTPB

Preliminary evaluations of the cis-2,3-dimethyl acyl aziridine curatives were carried out with the adipic acid (I) and trimesic acid (II) derivatives.



(I)



(II)

Gumstocks were prepared from the Butarez Type II prepolymer (as described previously in 1.2) at varying tri-/difunctional curative ratios. All the mixes were prepared at a COOH/aziridine ratio of one and were cured at 150°F.

After 4 days at 150°F only the 100% trifunctional curative gave a satisfactory cure. After 7 days at 150°F the gumstocks from the 75% tri/25 di and the 50% tri/50% di combinations were cured, but the gumstock from the 25% tri/75% di curative was not cured. After 14 days at 150°F the latter gumstock showed a low state of cure but the 100% difunctional curative gave no cure. The data on mechanical properties and cure of these gumstocks are summarized in Table XXXIII and the effect of tri/di-functional curative ratio on mechanical properties is shown in Figure 26. Mechanical properties were obtained as described in Section 1.2.

Figure 26

MECHANICAL PROPERTIES OF BUTAREZ TYPE II GUMSTOCKS
CURED WITH VARYING RATIOS OF TRI-/DI FUNCTIONAL
cis-2,3-DIMETHYL ACYL AZIRIDINES

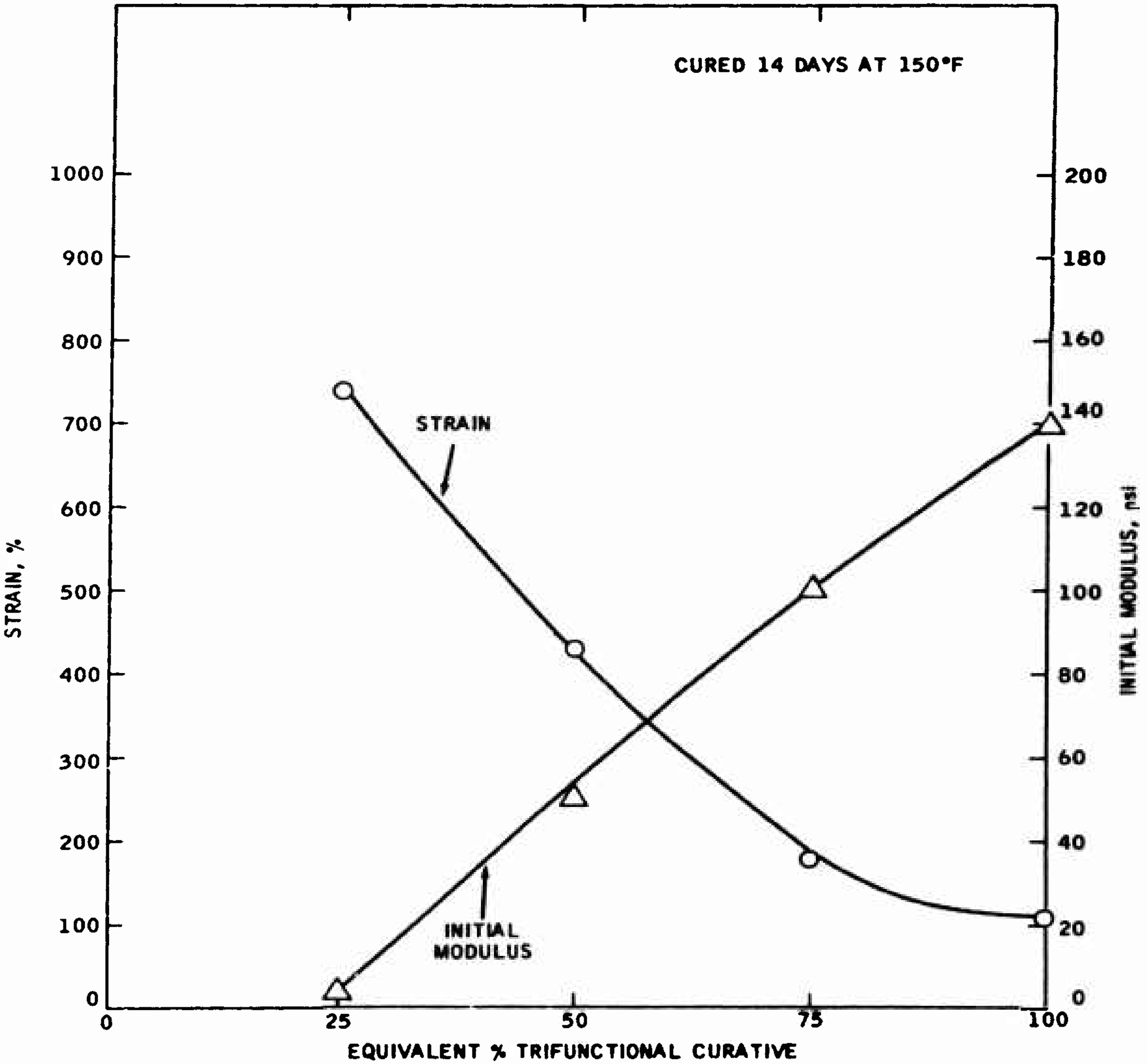


TABLE XXXIII

MECHANICAL PROPERTIES OF BUTAREZ TYPE II GUMSTOCKS CURED WITH TRI- AND DIFUNCTIONAL cis-2,3-DIMETHYL ACYL AZIRIDINES(1)

Curative System(2) Ratio Tri/Di-functional	Cure Cycle Days @ 150°F	Hardness, Shore A	Stress, psi	Strain, %	Initial Modulus, psi
100% Tri	4	43	90	360	60
100% Tri	14	53	150	160	140
75% Tri/25% Di	7	37	90	340	60
75% Tri/25% Di	14	48	110	180	100
50% Tri/50% Di	7	28	40	710	10
50% Tri/50% Di	14	36	130	430	50
25% Tri/75% Di	7	------------------ No cure ------------------			
25% Tri/75% Di	14	20	10	740	4
100% Di	14	------------------ No cure ------------------			
HX-868	4	35	70	200	60

(1) Butarez CTL Type II Lot #2278

(2) Trifunctional = derivative of trimesic acid
Difunctional = derivative of adipic acid

Further reaction occurs with additional cure time as evidenced by the greater hardness, higher stress, lower strain, and higher modulus values in all cases. Further work needs to be done to determine the optimum cure cycle for this system.

Several gumstocks were prepared with the *cis*-2,3-dimethyl acyl aziridine system using a different batch of Butarez Type II prepolymer. Significant differences in mechanical properties showed up between the two batches. These differences are readily apparent from the table below, even though the gumstocks were prepared at slightly different cure cycles.

TABLE XXXIV

MECHANICAL PROPERTIES OF GUMSTOCKS PREPARED FROM *cis*-2,3-DIMETHYL ACYL AZIRIDINES AND DIFFERENT BATCHES OF BUTAREZ TYPE II PREPOLYMER

Curative System Ratio Tri/Di Functional	Butarez Batch No.	Cure Cycle Days @ 150°F	Hardness, Shore A	Stress, psi	Strain, %
100% Tri	2278	4	43	90	360
100% Tri	2278	14	53	150	160
100% Tri	2285	6	47	170	160
25% Tri/75% Di	2278	7	----------	No cure	----------
25% Tri/75% Di	2278	14	20	10	740
25% Tri/75% Di	2285	6	29	130	560

Batch 2285 appears to reach a higher state of cure within a given time than Batch 2278. These differences will be minimized in the future by working with prepolymer from only one batch (2278).

4.3. Aging of Gumstocks at 275°F

Thermal aging of gumstocks was carried out at 275°F in a nitrogen atmosphere. Gumstock pads were placed in an oven that had a continuous flow of nitrogen through it. After a certain exposure time the small pads were removed and dumbbells cut for testing at ambient temperatures.

In one study a gumstock prepared from a completely trifunctional curative was aged for up to 14 days at 275°F. A summary of the mechanical properties of the aged samples is given below.

TABLE XXXV

MECHANICAL PROPERTIES OF BUTAREZ TYPE II GUMSTOCKS AGED AT 275°F IN NITROGEN ATMOSPHERE(1)

Curative	Days Aged at 275°F	Hardness, Shore A	Stress, psi	Strain, %	Initial Modulus psi
Tris-*cis*-2,3-Dimethyl Acyl Aziridine	0	43	90	360	60
	4	59	150	210	100
	7	48	170	210	140
	14	53	150	160	140
HX-868	0	35	70	200	60
	4	48	90	130	130
	7	42	90	120	130
	14	40	100	120	130

---

(1) Butarez CTL Type 2 Lot #2278; cured 4 days at 150°F.

Both curatives show a significant loss in strain values after 7 days aging at 275°F and both show an increase in stress after aging. The trifunctional 2,3-dimethyl acyl aziridine shows a greater increase in stress with aging which is a reflection of its lower state of cure after 4 days at 150°F. However, it must be remembered that HX-868 is not a completely trifunctional curative. At the reported equivalent weight of 142 (vs a theoretical equivalent weight of 123 for completely trifunctional material) HX-868 has a functionality slightly greater than 2.5. This corresponds in functionality to a mixture of 50% trifunctional and 50% difunctional curative.

In a second study where the <u>cis</u>-2,3-dimethyl acyl aziridine gumstocks were cured for a longer period there was very little degradation or change in mechanical properties after aging 4 days at 275°F.

TABLE XXXVI

MECHANICAL PROPERTIES OF BUTAREZ CTL GUMSTOCKS CURED WITH TRI- AND DIFUNCTIONAL ACYL-cis-2,3-DIMETHY L AZIRIDINES

(Cured 6 days @ 150°F)

Cure System (1)	Treatment After Cure (2)	Hardness, Shore A	Max. Stress, psi	Strain, %
100% Trifunctional	None	47	170	160
	1 day @ 275°F	47	150	130
	4 days @ 275°F	47	130	130
50% Trifunctional 50% Difunctional	None	20	90	720
	1 day @ 275°F	30	90	340
	4 days @ 275°F	35	80	200
HX-868	None	51	90	170
	1 day @ 275°F	61	120	160
	4 days @ 275°F	47	100	160
	14 days @ 275°F	51	110	130

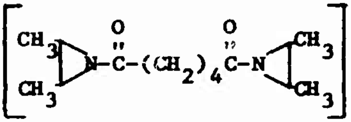
---

(1) Trifunctional = 2,3-dimethyl aziridine derivative of trimesic acid
Difunctional = 2,3-dimethyl aziridine derivative of adipic acid

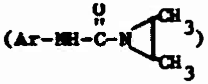
(2) Thermal aging in nitrogen atmosphere.

The trifunctional 2,3-dimethyl acyl aziridine gives a higher stress value than is obtained with the base case HX-868 but the strain values are essentially the same. This holds true for the aged samples also.

The 50/50 tri-difunctional curative gave a gumstock with the same stress as HX-868 but with a much greater strain value. With the 50/50 mixture there is a loss in strain on thermal aging and the stress value remained constant.

The substitution of a difunctional aliphatic acyl aziridine  for 50 percent of the trifunctional aziridine reduces the maximum stress level by a factor of about 2 but increases the strain capability by a factor of 4.5. Evaluation of this cure system in total propellants will ultimately determine whether the pure trifunctional acyl aziridine or the mixed di-/trifunctional cure system will impart optimum properties to the propellant.

D. SYNTHESIS AND EVALUATION OF N-CARBAMYL AZIRIDINE (UREA) CURATIVES

N-carbamyl aziridine systems are being studied as curatives for carboxy acids as another approach to increasing the rate of cure while retaining the selectivity for the addition reaction with acids. Replacing the N-substituent with a less electron withdrawing group should increase the rate of reaction. The N-carbamyl ureido derivatives () react faster with acids than does HX-868. In addition they appear to have good selectivity.

Gumstock studies have been made with combinations of tri- and difunctional, aromatic and aliphatic curatives. Three trifunctional and two difunctional N-carbamyl aziridine curatives have been evaluated so far. The initial studies indicate that the aliphatic materials cure faster than the aromatic curatives. Of the trifunctional curatives the most promising has been the carbamyl *cis*-2,3-dimethyl aziridine derivative of cyclohexane.

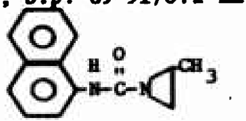
Preliminary evaluation of the aziridinyl ureido curatives in propellants has been initiated, but insufficient data is available for extensive discussion at this time.

1. Synthesis and Evaluation of Monofunctional N-Carbamyl Aziridines

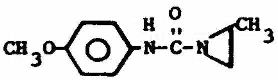
N-carbamyl aziridine derivatives were synthesized by reacting at 0°C an isocyanate with an aziridine in benzene or ether solution. Essentially quantitative yields were obtained in each case when stoichiometric quantities were used.

Compound I was synthesized from 1-naphthyl isocyanate and 1-methyl aziridine; compound II was synthesized from p-methoxyphenylisocyanate and 1-methylaziridine, and compound III was synthesized from p-tolueneisocyanate and *cis*-2,3-dimethyl aziridine. Compounds I and III were recrystallized to a constant melting point. NMR and I.R. data were consistent with the structures. Table XXXVII shows the results.

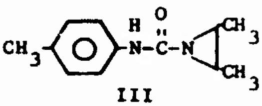
Compound IV, the only totally aliphatic derivative, was made from n-butyl isocyanate and cis-2,3-dimethyl urea. This compound was a distillable liquid; b.p. 89-91/0.2 mm.



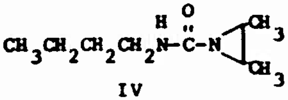
I



II



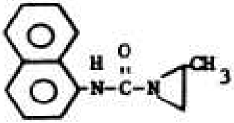
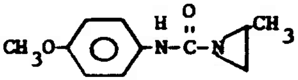
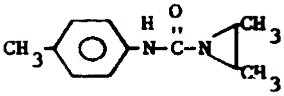
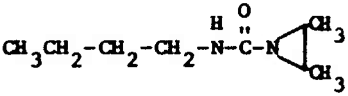
III



IV

TABLE XXXVII

MONOFUNCTIONAL N-CARBAMYL AZIRIDINE COMPOUNDS

Compound	M.p. °C	Yield, %	Meq. Aziri./g Sample[(a)]	
			Actual	Found
	115-116	83	--	--
	80-81	75	4.85	4.72
	104-105	36		
	(89-91/ 0.2mm)(b)	83	--	--

---

(a) Miliequivalents of aziridine nitrogen/g sample = 14/Mol. wt. of sample

(b) b.p.

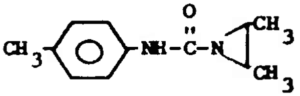
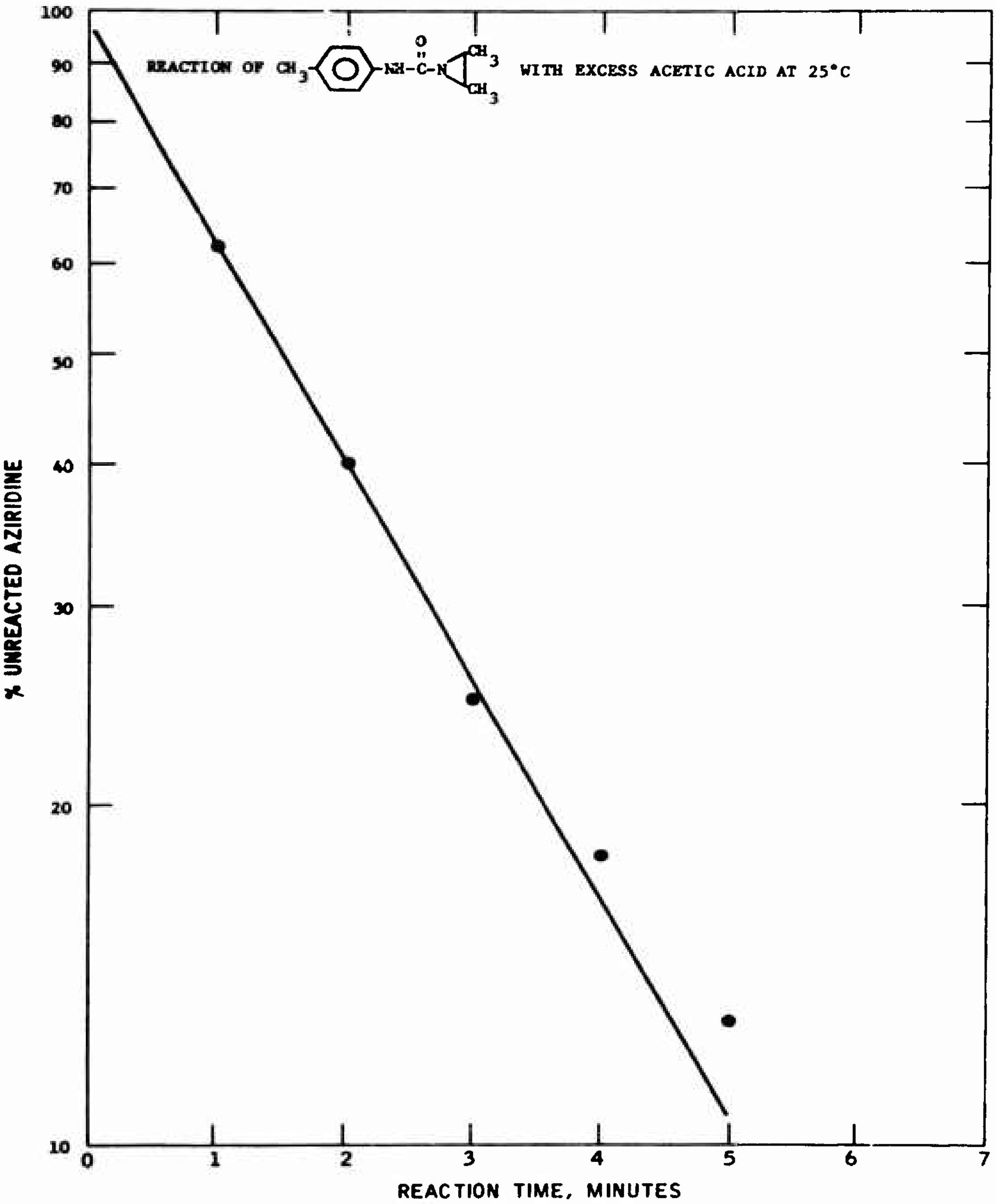
The reaction of N-[p-tolyl carbamyl]-cis-2,3-dimethyl aziridine  with excess acetic acid was studied at room temperature. The reaction was very rapid as shown in Figure 27, and had a half-life of 1 minute 30 seconds. There is little to distinguish this reaction from the reactions of the acyl aziridines with acetic acid, however, so the reaction rate of the N-carbamyl substituted compound was studied with octanoic acid in toluene at 150°F.

FIGURE 27


REACTION OF CH3-C6H4-NH-C(=O)-N(aziridine)(CH3)(CH3) WITH EXCESS ACETIC ACID AT 25°C
% UNREACTED AZIRIDINE
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
REACTION TIME, MINUTES

As in the previous runs the reaction of the N-[p-tolyl carbamyl]-cis-2,3-dimethyl aziridine with octanoic acid was run at an acid/aziridine ratio of 1, 10% concentration in toluene, at 150°F. The reaction was monitored by following the disappearance of acid by titration with tetrabutyl ammonium hydroxide. Figure 28 shows that the rate is considerably faster than the rate for the corresponding reaction with HX-868. The half-life for the N-carbamyl compound is 4 hours vs a half-life of 58 hours for HX-868. This faster rate suggests that pot-life problems could be a problem with the N-carbamyl curatives.

The reaction of the N-carbamyl compound with octanoic acid was also examined in the presence of ammonium perchlorate. Ammonium perchlorate was added to the toluene solution described above at a level of 5% based on the total solution. The reaction was monitored as above by titrating for octanoic acid with tetrabutyl ammonium hydroxide.

TABLE XXXVIII

REACTION OF N-[p-TOLYL CARBAMYL]-cis-2,3-DIMETHYL AZIRIDINE WITH OCTANOIC ACID IN THE PRESENCE OF AMMONIUM PERCHLORATE(1)

	% Unreacted Acid	
Reaction Time	No AP Present	AP Present
20 hours	18.1	24.6
29 hours	15.6	23.7
48 hours	12.6	24.8

---

(1) 10% concentration of reactants in toluene; 5% AP based on total solution.

Unlike the case of HX-868 where the AP appeared to have no effect on the rate of reaction, here it slows the rate of reaction slightly and may even cause a slight amount of side reaction to occur as evidenced by a leveling off at around 24% acid remaining.

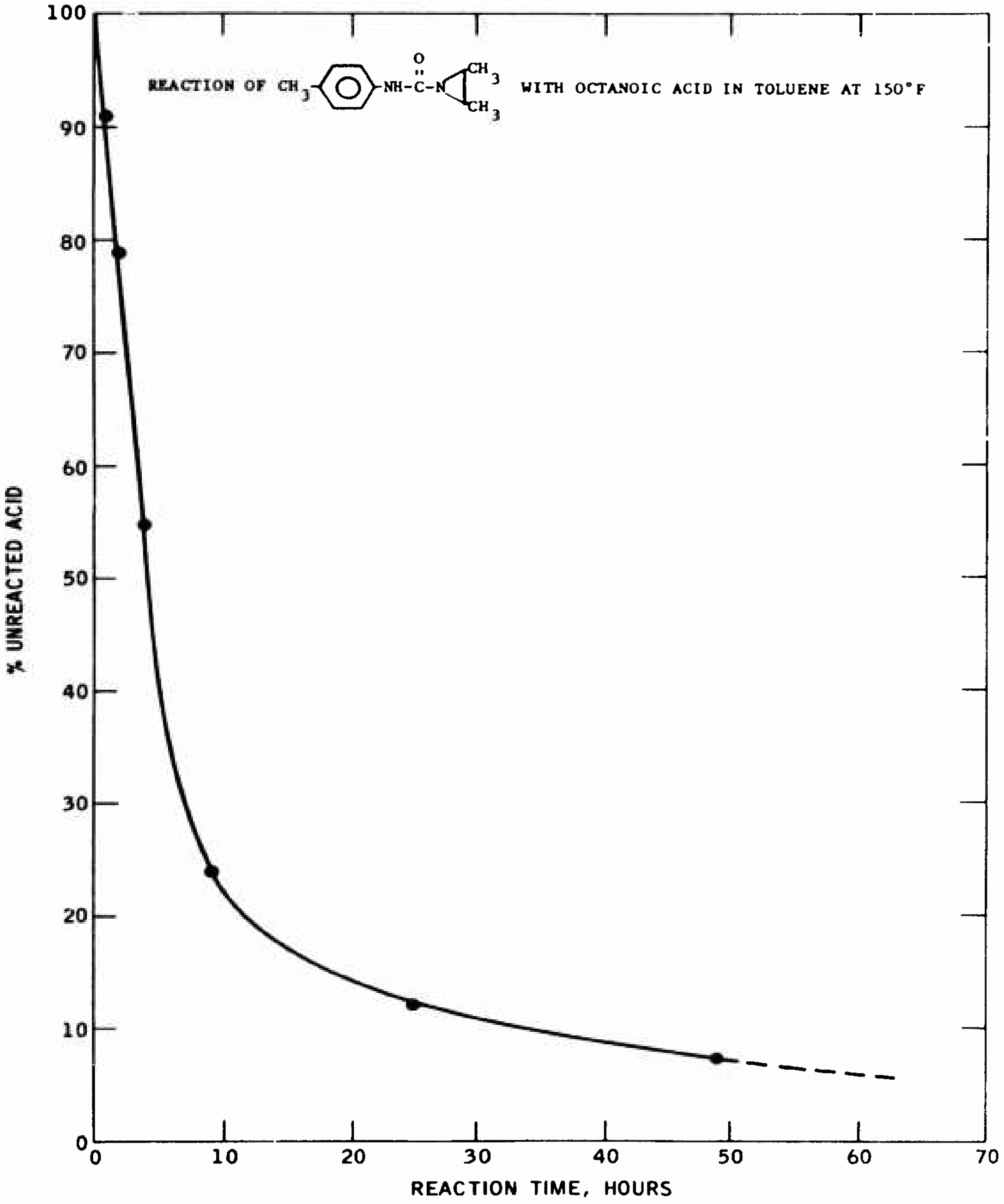
2. Synthesis of Di and Trifunctional Curatives Based on cis-2,3-Dimethyl Aziridine

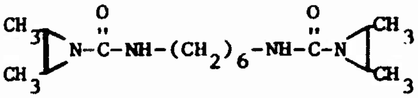
2.1. Synthesis of Difunctional N,N'-Aliphatic and Aromatic Carbamyl Aziridines

a. N,N'-Hexamethylene Bis[-(carbamyl cis-2,3-dimethyl aziridine)] (V)

Compound V was prepared in a high yield by reacting freshly distilled cis-2,3-dimethyl aziridine with freshly distilled hexamethylene diisocyanate. The crude product (93% of theory) was recrystallized from hot methanol-acetone, m.p. 120-120.5°C. The IR is shown in Appendix C4. Elemental analyses are within 0.7% of theory. The NMR spectrum is consistent with the proposed structure.

FIGURE 28


REACTION OF CH3 NH-C-N CH3 CH3 WITH OCTANOIC ACID IN TOLUENE AT 150°F
O
% UNREACTED ACID
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
REACTION TIME, HOURS

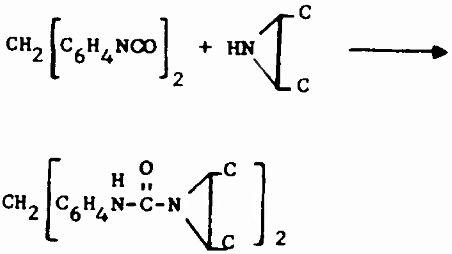


(V)

b. 4,4'-Bis[-(cis-2,3-Dimethylaziridinyl) Carbamyl] Diphenyl Methane (VI)

A difunctional curative (VI) was made according to Equation 1 using purified diphenylmethane diisocyanate. Essentially quantitative yields were obtained: m.p. 182-184°C. Neut. equiv. on the material was 4.97 meq. N/g sample; theor., 5.10. Infrared and NMR spectra are shown in Appendix C4 and C7, respectively.

(1)

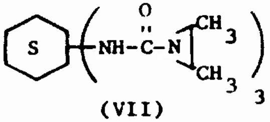


(VI)

2.2. Synthesis of Trifunctional N,N',N"-Carbamyl Aziridines

a. 1,3,5-Cyclohexane tris carbamyl cis-2,3-dimethyl aziridine (VII)

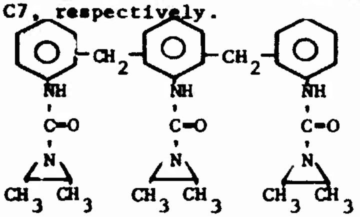
Compound VII was prepared in 99% crude yield by reacting cis-2,3-dimethylaziridine with freshly distilled cyclohexane triisocyanate in benzene solution. The cyclohexane triisocyanate starting material was kindly made available to this program by Aerojet-General Corporation. Recrystallization from methylene chloride-hexane system gave VII in 90% yield, m.p. 200-202°C. Infrared spectrum and NMR are shown in Appendix C4 and C7, respectively.



(VII)

b. 1,1',1"-Tris[carbamyl(cis-2,3-dimethylaziridine)] Triphenylene Dimethylene (VIII)

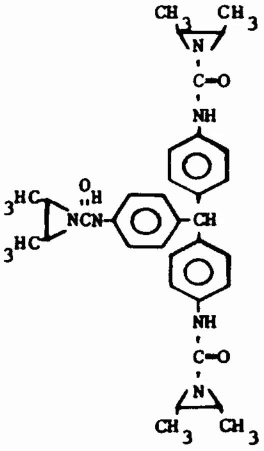
Freshly distilled triphenyl dimethylene triisocyanate was reacted with cis-2,3-dimethyl aziridine in benzene solution at 0°C. The product was isolated in quantitative yield. Infrared and NMR spectra are shown in Appendix C4 and C7, respectively.



(VIII)

c. 1,1',1"-Tris[carbamyl(cis-2,3-dimethylaziridine)] Triphenyl Methane (IX)

The titled compound (IX) was prepared by reacting purified tris-[p-isocyanatophenyl]methane (TTI) with cis-2,3-dimethyl aziridine with similar techniques described above. Relatively pure tris-[p-isocyanatophenyl]-methane required for this reaction was obtained from the impure commercial grade TTI by precipitation with pentane. All attempts to use the commercial grade TTI without purification gave an impure (IX) which could not be purified. The curative melted at 142-145°C. Infrared and NMR spectra are shown in Appendix C4 and C7.



(IX)

3. Evaluation of Di- and Trifunctional Carbamyl Aziridine Curatives in Butarez CTL Type II Gumstocks

The N-carbamyl aziridine compounds described above were evaluated as curatives for carboxy-terminated polymers with Butarez CTL Type II prepolymer. Gumstocks were prepared at COOH/aziridine equivalent ratios of 1 and cured at 150°F. Various combinations of the trifunctional and difunctional curatives were examined to try to determine the best aziridinyl ureido system and to establish a good cure cycle.

3.1. Trifunctional Carbamyl Aziridine Curative Studies

Initial work with the three trifunctional curatives showed that the aromatic derivatives do not cure as rapidly as the cyclohexane derivative. In addition, the triphenylene dimethylene derivative has much lower solubility in the polymers than the other compounds. Even at 150°F the triphenylene dimethylene derivative was not completely miscible when used as the sole curative (with no difunctional curative present).

At 150°F the cyclohexane derivative gave a good cure with the Butarez prepolymer in 4 days but the aromatic materials did not cure. It took 7 days curing at 150°F to get a reasonable cure with the triphenylene dimethylene derivative (Table XXXIX), but even at this stage the curative did not appear to be completely miscible. After 10 days cure at 150°F the triphenyl methane derivative showed only a low state of cure.

TABLE XXXIX

BUTAREZ CTL GUMSTOCKS CURED WITH TRIFUNCTIONAL N-CARBAMYL cis-2,3-DIMETHYL AZIRIDINE CURATIVES

Curative System	Cure Period at 150°F	Stress, psi	Strain, %	Initial Modulus, psi
Cyclohexane Derivative	4 days	320	250	280
Triphenylene Dimethylene Derivative	4 days	------------	No cure	------------
	7 days	100	130	
Triphenylmethane Derivative	4 days	------------	No cure	------------
	7 days	10	80	10
	10 days	20	100	20

The faster cure rate of the cyclohexane derivative is quite clear. However, a completely trifunctional curative system would give a binder that is too tightly crosslinked, so combinations of trifunctional and difunctional curatives are needed.

A series of gumstocks were prepared from Butarez with varying mixtures of tri-/difunctional carbamyl aziridine curatives to study the effect of tri/difunctional curative ratio on properties, as well as to study the effect of aromatic and aliphatic structures on cure rate and mechanical properties. Table XL lists the data for the cyclohexane trifunctional curative and Table IXL lists the data for the triphenylene dimethylene trifunctional curative.

The slower rate of cure of the aromatic trifunctional curative shows up very well. Gumstocks prepared with this curative were cured for 14 days vs 4 days for the alicyclic trifunctional curative. Even with the longer cure time the aromatic derivative did not give good cures and the gumstocks had much poorer mechanical properties than the corresponding gumstocks prepared with the alicyclic curative.

Figure 29

MAXIMUM STRESS PROPERTIES OF BUTAREZ GUMSTOCKS CURED WITH VARYING RATIOS OF TRI/DI-FUNCTIONAL N-CARBAMYL AZIRIDINE CURATIVES

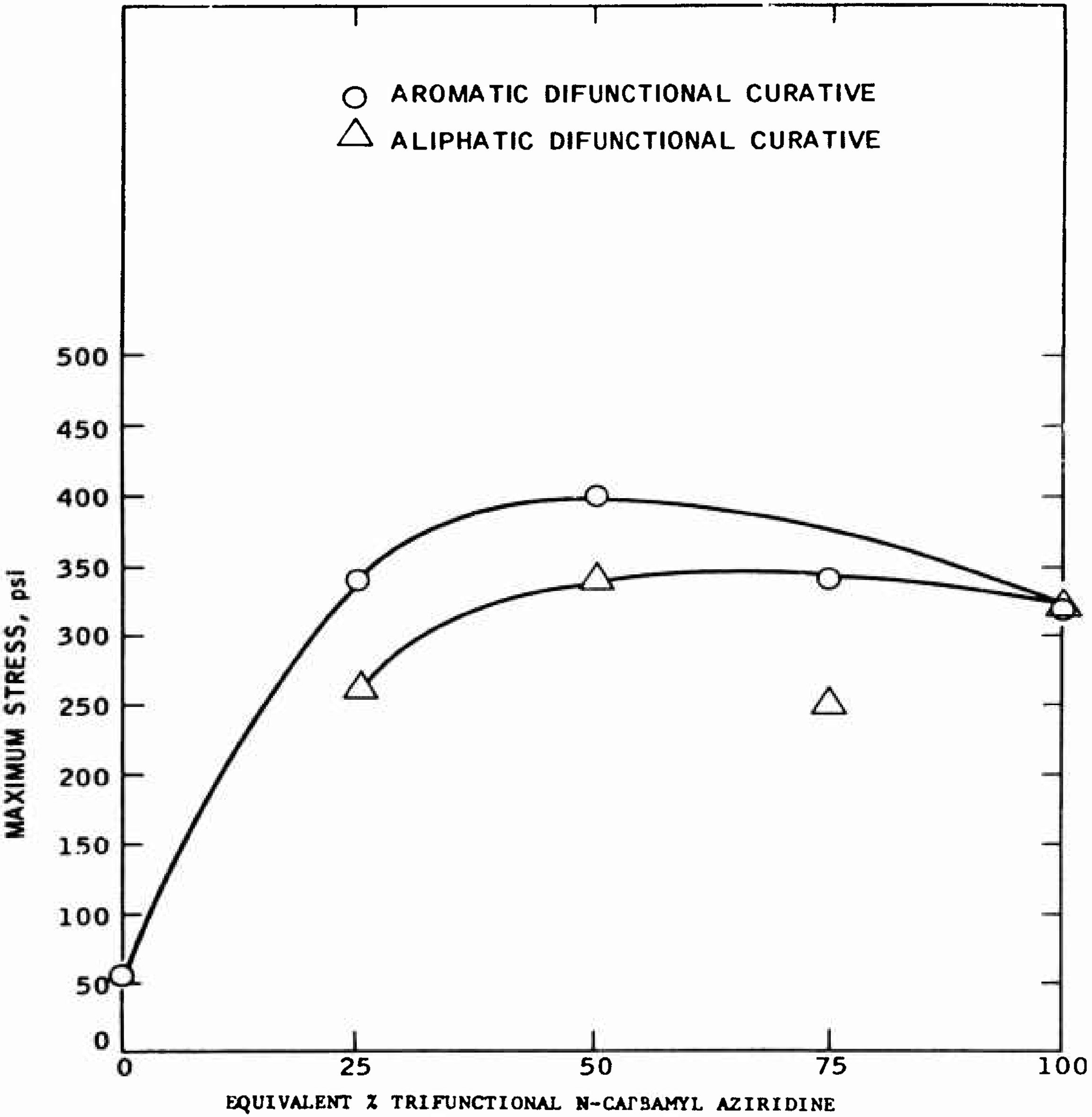


Figure 30

MAXIMUM STRAIN PROPERTIES OF BUTAREZ GUMSTOCKS CURED WITH VARYING RATIOS OF TRI/DI-FUNCTIONAL N-CARBAMYL AZIRIDINE CURATIVES

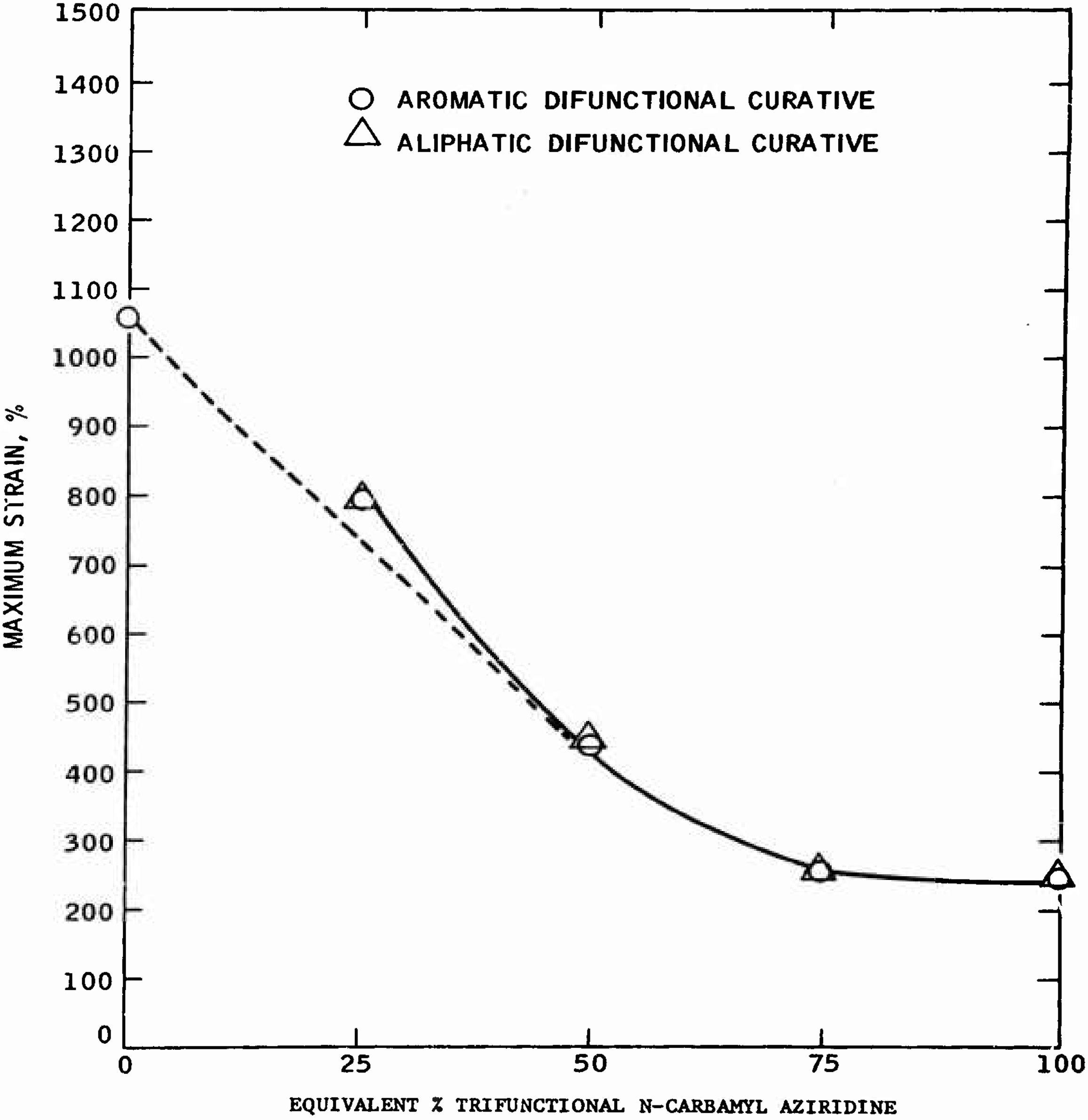
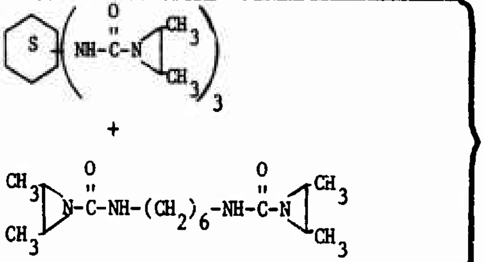
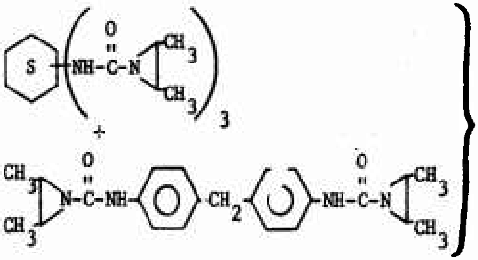


TABLE XL

MECHANICAL PROPERTIES OF BUTAREZ CTL GUMSTOCKS CURED WITH N-CARBAMYL AZIRIDINE CURATIVES(1)

Curing System	Ratio Tri/Di	Hardness Shore A	Max. Stress psi	Strain, %	Initial Modulus, psi
	0/100	45	40	1040	60
	25/75	43	260	800	80
	50/50	52	340	450	160
	75/25	60	250	260	200
	100/0	60	320	250	290
	0/100	42	50	1060	40
	25/75	51	340	800	130
	50/50	51	400	440	210
	75/25	56	340	260	260
	100/0	60	320	250	290

---

(1) Cured 4 days @ 150°F; Reported values are an average of 3 samples.

TABLE IXL

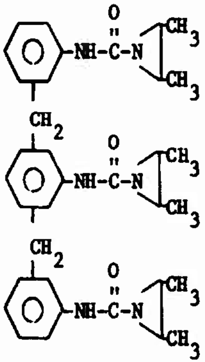
MECHANICAL PROPERTIES OF BUTAREZ CTL GUMSTOCKS CURED WITH N-CARBAMYL AZIRIDINE CURATIVES(1)

Curing System(2)	Ratio Tri/Di	Hardness, Shore A	Stress, psi	Strain, %	Initial Modulus, psi
Tris-triphenylene dimethylene/bis-hexamethylene derivative	25/75	48	10	690	10
	50/50	33	40	220	30
	75/25	43	40	120	50
Tris-triphenylene dimethylene/bis-diphenylmethane derivative	25/75	51	120	380	100
	50/50	47	90	190	90
	75/25	45	60	140	60

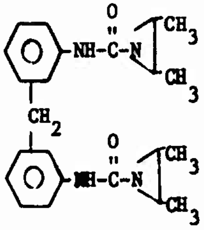
---

1. Cured 14 days at 150°F; reported values are an average of 3 samples

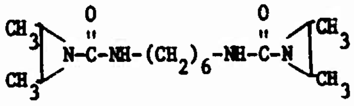
2.



Triphenylene
Dimethylene
Derivative



Diphenylmethane
Derivative



Hexamethylene Derivative

3.2. Effect of Di/Trifunctional Ratio on Mechanical Properties of Gumstocks

The gumstocks prepared with the cyclohexane trifunctional curative were used to study the effect of the difunctional curative. At every level the aromatic difunctional curative gives a higher stress (Figure 29). The strain values essentially follow the same curve for both the aliphatic and aromatic difunctional curative (Figure 30). This same independence of maximum strain on the structure of the difunctional curative has been observed for the isocyanate cured OH-Telagen-S. The aromatic curative also gives a higher modulus at all levels (Figure 31). This is not surprising because it is less flexible than the aliphatic curative and should produce a stiffer chain. The lower modulus should make the aliphatic system the preferred curative for propellant binders.

As anticipated the strain values decreased with increasing trifunctional aziridine level, and stress, modulus and hardness values increased with increasing trifunctional curative. These effects will have to be studied further in propellant mixes to establish the best di/trifunctional ratio. It is a little surprising that the difunctional curatives give gumstocks with fairly good properties at ambient temperatures This may possibly be due to hydrogen bonding in the system.

3.3. Butarez Batch Differences

The above values were obtained with a new batch of Butarez (Lot No. 2278). These values differ quite a bit from the properties of the gumstocks prepared from another batch of Butarez (Lot No. 2285) even though there is very little difference in the equivalent weights of the two samples (2680 vs 2710). The difference in the two batches can be seen from the differences in the gumstock properties listed below.

TABLE VIII

EFFECT OF BUTAREZ LOT VARIATIONS ON MECHANICAL PROPERTIES OF GUMSTOCKS CURED WITH N-CARBAMYL AZIRIDINE CURATIVES(1)

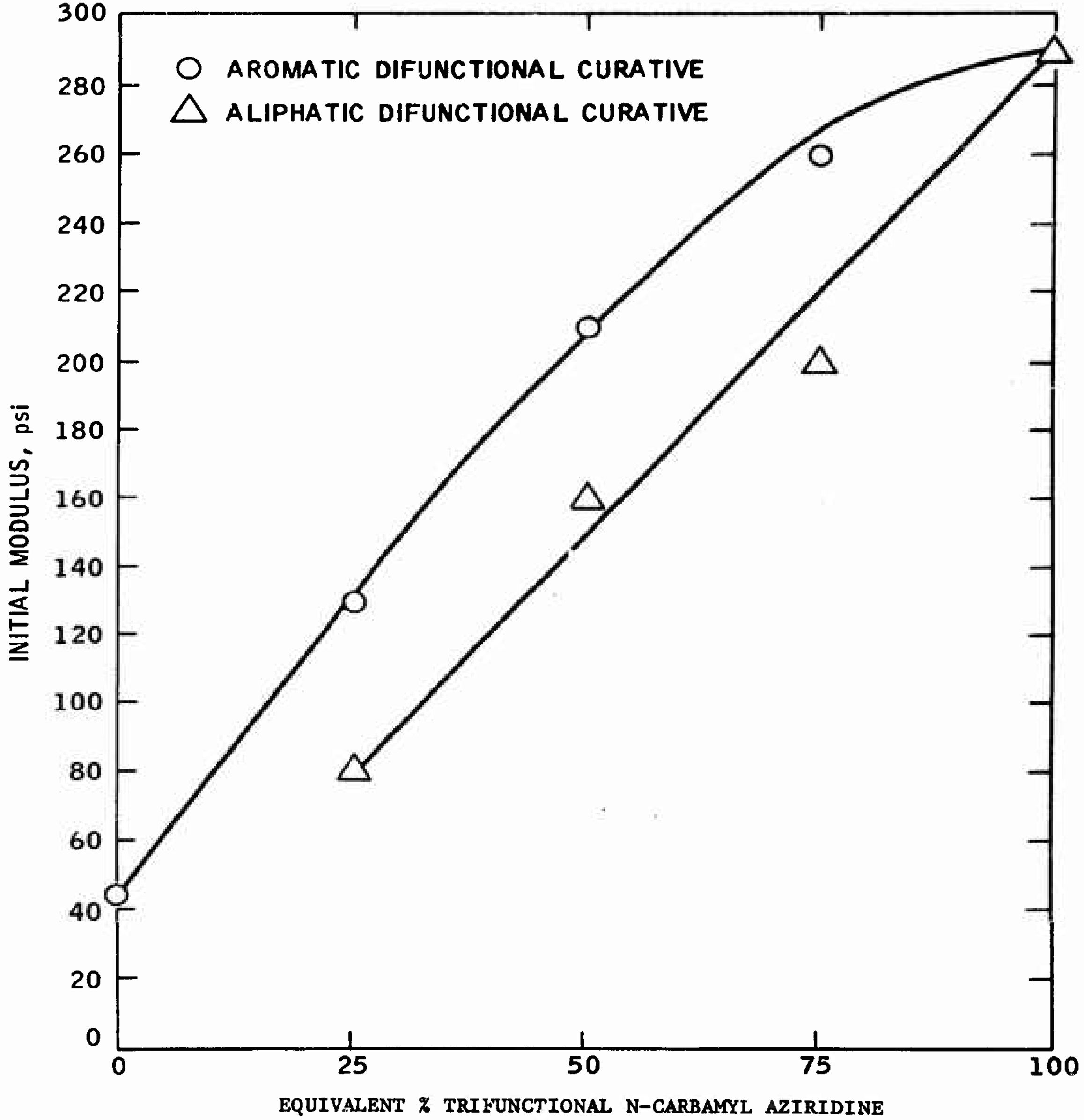
Butarez Sample	Curative Ratio Tri/Di	Hardness Shore A	Max. Stress, psi	Strain, %	Initial Modulus, psi
2285	25/75	46	220	470	130
2278	25/75	43	260	800	80
2285	50/50	62	330	360	230
2278	50/50	52	340	450	160
2285	75/25	55	320	220	310
2278	75/25	60	250	260	200
2285	100/0	64	160	200	150
2278	100/0	60	320	250	290

---

(1) Cured 4 days @ 150°F; Alicyclic trifunctional and aliphatic difunctional curative; Reported values are an average of three samples

Figure 31

INITIAL MODULUS OF BUTAREZ GUMSTOCKS CURED WITH VARYING RATIOS OF TRI/DI-FUNCTIONAL N-CARBAMYL AZIRIDINE CURATIVES



The stress and strain values are higher for Lot No. 2278 and the modulus values are lower except for the 100% trifunctional curative.

3.4. Mechanical Properties After Heat Aging at 180°F and 275°F in a Nitrogen Atmosphere

Thermal aging studies were carried out with Butarez-carbamyl aziridine gumstocks at 275°F in a nitrogen atmosphere. The effect of thermal aging on strain properties is shown in Figure 32. A summary of the effect of thermal aging on mechanical properties is given in Table VIII.

TABLE VIII

MECHANICAL PROPERTIES OF BUTAREZ CARBAMYL AZIRIDINE GUMSTOCKS AT AMBIENT TEMPERATURE AFTER HEAT AGING AT 275°F(1)

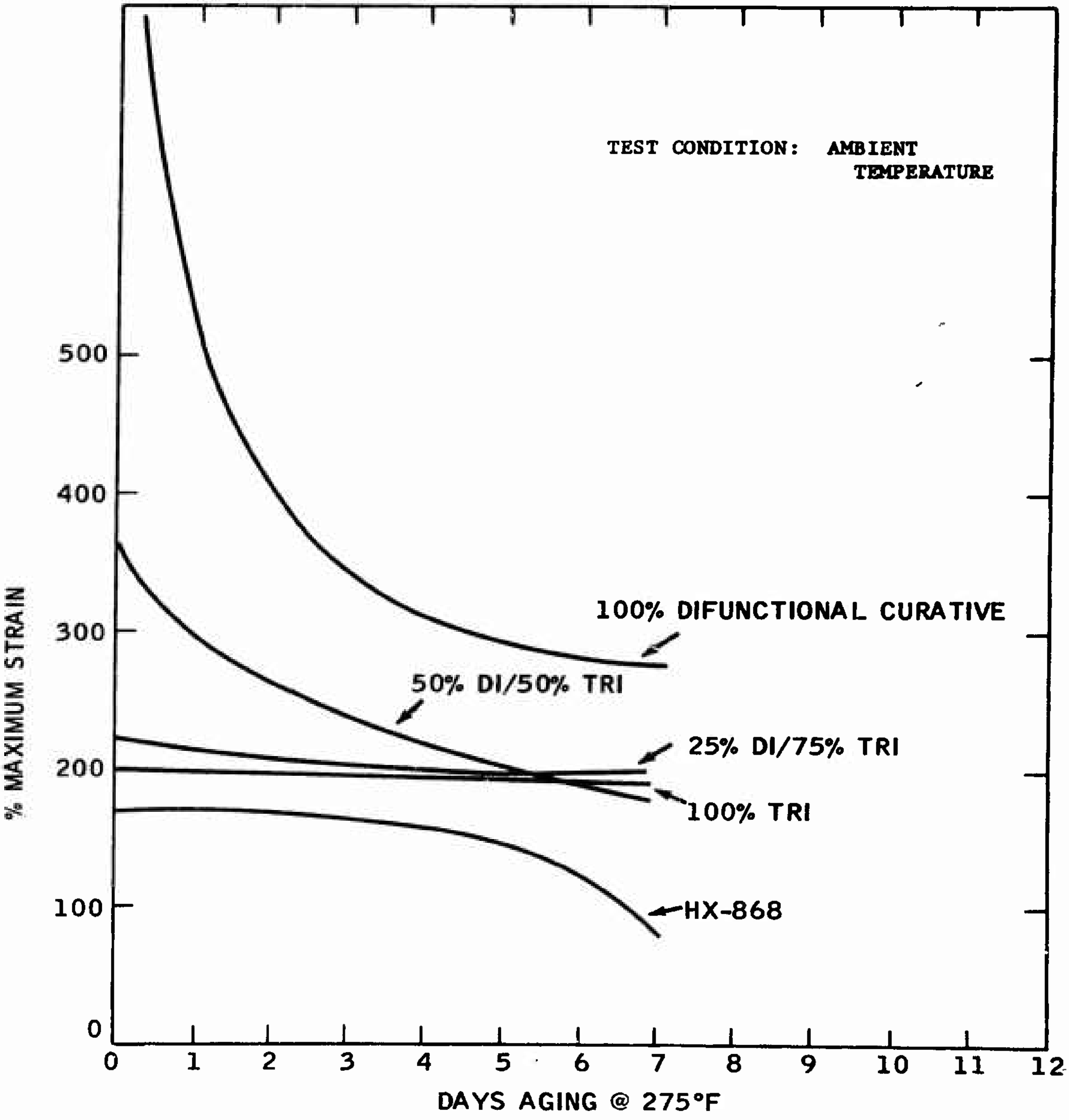
Tri/Difunctional Curative Ratio	Days Aged @ 275°F	Stress, psi	Strain, %	Initial Modulus, psi
0/100	None	280	950	100
	1	210	510	70
	4	120	310	70
	7	120	280	70
25/75	None	220	470	130
	1	140	280	100
	4	50	190	40
	7	40	60	80
50/50	None	330	360	230
	1	130	210	100
	4	100	220	80
	7	90	190	80
25/75	None	320	220	310
	1	240	170	260
	4	230	200	220
	7	210	200	200
0/100	None	160	200	150
	1	230	150	260
	4	260	170	290
	7	200	190	190

---

(1) Cured 4 days at 150°F; alicyclic trifunctional and aliphatic difunctional curative; results are an average of 3 samples.

Figure 32

STRAIN PROPERTIES OF BUTAREZ N-CARBAMYL AZIRIDINE GUMSTOCKS AGED AT 275°F IN NITROGEN ATMOSPHERE



At low levels of trifunctional curative there is a steep decline in stress and strain with aging at 275°F. This may be due to chain breaking or a reduction in hydrogen bonding. At the higher levels of trifunctional curative there is very little degradation in properties and the gumstocks appear to retain their properties much better than the HX-868 cured gumstock. The thermal aging data indicate that trifunctional curative levels of greater than 50% are needed for good gumstock properties.

Aging at 275°F is quite severe and the lower crosslinked systems suffer the most. To determine if this was too severe a condition for thermal aging, several systems containing low trifunctional curative levels were aged at 180°F for longer periods. These results are listed in Table VIL.

TABLE VIL

MECHANICAL PROPERTIES OF BUTAREZ-CARBAMYL AZIRIDINE GUMSTOCKS AGED AT 180°F AND 275°F(1)

Tri/Difunctional Curative Ratio	Treatment After Cure	Hardness, Shore A	Stress, psi	Strain, %
20/80	None	51	250	350
	1 week @ 180°F	56	260	330
	2 weeks @ 180°F	55	260	300
	5 weeks @ 180°F	53	230	220
10/90	None	53	270	510
	1 week @ 180°F	53	260	430
	1 day @ 275°F	43	140	330
	4 days @ 275°F	35	90	240
25/75	None	53	280	370
	1 week @ 180°F	57	260	240
	1 day @ 275°F	--	220	340
	4 days @ 275°F	41	110	270

---

(1) Cured 6 days at 150°F; alicyclic trifunctional and aliphatic difunctional curative; results are an average of 3 samples.

The results show that one day aging at 275°F is considerably more severe than one week at 180°F. In the case of the 20/80 system no significant change was noted in properties until after 5 weeks aging at 180°F. For this reason most of the future screening work will be done at higher temperatures.

4. Evaluation of Di- and Trifunctional Carbamyl Aziridine Curatives in COOH-Telagen-S Gumstocks

Gumstock studies with COOH-Telagen-S prepolymer have been limited because of a shortage of prepolymer. However, preliminary experiments have been conducted to compare the properties of the saturated Telagen polymer with Butarez. In one experiment gumstocks were prepared from the two prepolymers at stoichiometric ratios of carboxy/aziridine with a curative system composed of 25% 1,3,5-cyclohexane tris carbamyl cis-2,3-dimethyl aziridine and 75% N,N'-hexamethylene bis-carbamyl, cis-2,3-dimethyl aziridine.

After 24 hours cure at 150°F, the Butarez system had cured to set and had very slight tack, while the Telagen system was still extremely tacky. After 48 hours the Butarez sample was almost tack free and was removed from the oven. The Telagen sample was still quite tacky after 48 hours and was cured for 5 days before it became almost tack free. Mechanical properties of the cured samples are listed below.

TABLE VL

MECHANICAL PROPERTIES OF COOH-TELAGEN-S AND BUTAREZ CTL GUMSTOCKS CURED WITH CARBAMYL cis-2,3-DIMETHYL AZIRIDINES(1)

Prepolymer	Cure, Days	Hardness Shore A	Maximum Stress, psi	Strain, %	Initial Modulus, psi
Butarez CTL Type II	2	52	260	600	120
COOH-Telagen-S	5	55	140	1110	110

---

(1) Cured at 150°F - Ratio 25/75 tri-/difunctional aziridine

The Butarez system cures considerably faster than the COOH-Telagen-S prepolymer. Also there is a significant difference in the stress and strain levels of the two gumstocks which may reflect the higher molecular weight of the Butarez prepolymer.

Gumstocks were also prepared from the satureated Telagen carboxy polymer using several combinations of carbamyl aziridine curatives. Again the gumstocks were prepared at stoichiometric ratios of carboxy/aziridine and a ratio of 25 tri/75 difunctional curative. Mechanical properties of the cured samples are listed below.

TABLE VIL

MECHANICAL PROPERTIES OF COOH-TELAGEN-S GUMSTOCKS CURED WITH CARBAMYL cis-2,3-DIMETHYL AZIRIDINES

Cure System(1)	Hardness, Shore A	Stress, psi	Strain, %	Initial Modulus, psi
Tris-cyclohexane/bis-hexamethylene	55	140	1110	110
Tris-cyclohexane/bis-diphenylmethane	58	270	470	
Tris-triphenylene dimethylene/bis-diphenylmethane	----------- Soft-Tacky-Porous -----------			

---

(1) Tri/difunctional curative ratio = 25/75
Cured 5 days at 150°F.

As in the case with the Butarez prepolymer the aromatic difunctional curative gave a system with higher stress. In this case, however, the aliphatic system gave a considerably greater strain value (unlike the Butarez system where the strain values appeared to be independent of the aliphatic or aromatic character of the difunctional curative). This may be a reflection of the lower molecular weight of the Telagen polymer which gives the cure linkage a greater effect on mechanical properties. The completely aromatic system did not cure, probably because of poor dispersion of the trifunctional curative in the polymer.

5. Preliminary Evaluation of Ureido Aziridines in Telagen CT Propellants

Evaluation of two carbamyl aziridine curatives in propellants has been initiated by Lockheed. Three propellant batches were made, two with Butarez CTL and one with a lot of Telagen CT available at LPC, since the base prepolymers had not yet been received. The propellant formulation data are summarized in Table IIL.

In contrast to HX-868 which is a viscous oil soluble in the binder system, the carbamyl aziridines are high melting solids, more difficulty soluble in the binders. Batch A in Table IIIL was formulated with the cyclohexane carbamyl aziridine. The latter was added early in the mix cycle, and blended with prepolymer and non-functional polybutadiene plasticizer. The oxidizer was blended in increments, and final mix temperature was 136°F. Apparent thickening was noted during vacuum casting of the propellant, indicating a potential pot life problem. Total mix time for batch A was 55 minutes. The second propellant, B in Table IIIL was formulated with a 50/50 ratio of di/trifunctional aziridines, at the same total imine to carboxy ratio used in batch A, 0.85/1.0. The solid curatives were added last, and mixed with all of the other propellant ingredients for 20 minutes at 130-140°F. Again the propellant viscosity was excessive, as a result of incipient cure. Although the curatives are not soluble in the polybutadiene plasticizer, they can be well-dispersed in it. In Batch C, Table IIIL, the curatives were added last as a slurry in one-fourth of the total polybutadiene, and mixing time was 15 minutes at 120-133°F. Propellant viscosity was lower than the previous two cases, indicating that this technique should be useful.

TABLE IIIL

PROPELLANTS MADE WITH CARBAMYL AZIRIDINES(a)

No. A45-04	A	B	C
Solids, weight-%	86.5	86.5	86.5
ZL-496 Polybutadiene	3.5	3.5	3.5
Triaziridine(b)	0.442	0.221	0.205
Diaziridine(c)	--	0.243	0.227
Butarez CTL	9.558	9.536	--
Telagen CT	--	--	9.568
Curative addition	early-solid	late-solid	late-solid
Imine/COOH	0.85/1.0	0.85/1.0	0.85/1.0
Diaziridine/triaziridine	0/100	50/50	50/50
End of mix viscosity, Kps/°F	>100/115°F	>100/120°F	45/105°F

(a) 500-gram batches mixed at 20 rpm in one pint vertical mixer.

(b) 1,3,5-cyclohexane carbamyl-cis-2,3-dimethyl aziridine

(c) N,N'-hexamethylene bis carbamyl-cis-2,3-dimethyl aziridine

When the Telagen CT ordered for the current program arrived, four propellant batches were formulated with the aziridines as follows:

Formulation	Aziridine/Carboxyl Equivalents Ratio	Di/Trifunctional Equivalence Ratio
1	.85	9/1
2	.85	3/1
3	.85	1/1
4	.70	1/1

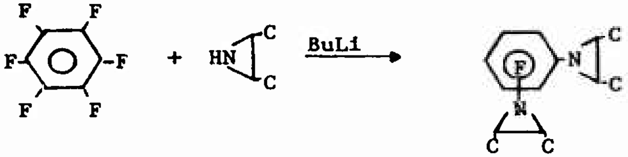
In all of these the curatives were dispersed in the non-functional polybutadiene and added at the end of mixing. In (2) the curative incorporation time was 10 minutes at 130-135°F. Incipient cure occurred and the propellant had to be hand-packed into the container. In (3) and (4) the temperature was reduced to 107-110°F during curative incorporation (15 minutes). No casting problem was encountered. Reducing the curative to carboxy ratio in (4) did not appear to help pot life. Formulations (1), (2), and (4) did not cure adequately in 5 days at 140°F, and are being subjected to additional cure. Formulation (3) was well-cured after 5 days and tensile properties are being determined.

E. SYNTHESIS AND EVALUATION OF FLUOROBENZENE AZIRIDINE CURATIVES

A small quantity of p-[bis-(cis-2,3-dimethyl aziridine)-]tetrafluoro benzene was synthesized by reacting the preformed lithio cis-2,3-dimethyl aziridine with perfluorobenzene (Equation 1).

The compound melted at 135-136°C (recrystallized from methanol) and had an elemental analysis which checked for $C_{14}H_{20}N_2F_4$. Examination of the proton NMR showed the presence of the cis-2,3-dimethyl aziridine moiety. F^{19} NMR showed it to be the para isomer (singlet). The IR is shown in Appendix C8.

(1)



The compound, although high melting, was readily soluble in many organic solvents including, in particular, paraffinic hydrocarbons. This may have some implications in finding a material which although solid will have good solubility in the carboxy prepolymers.

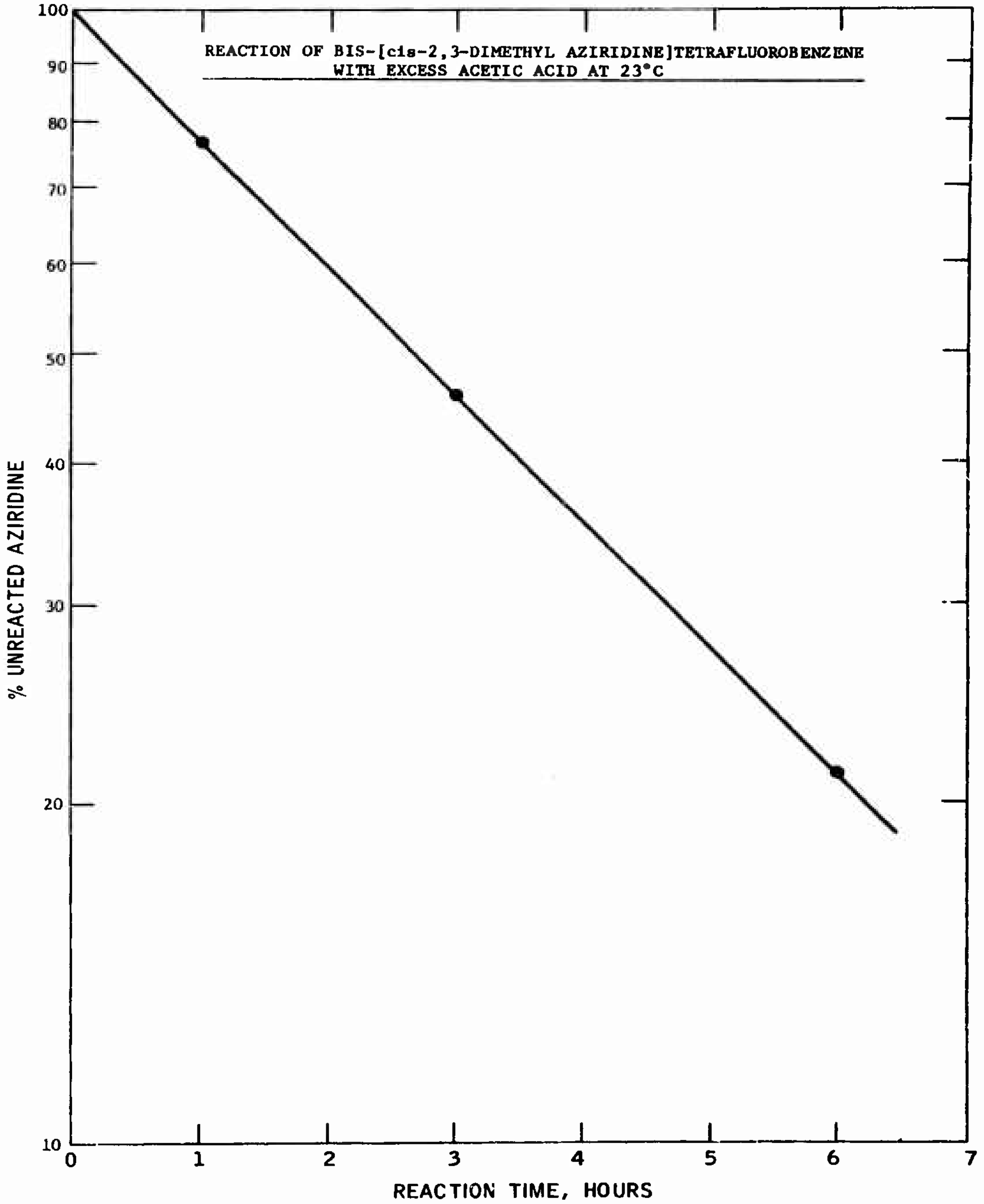
The reaction of bis-[cis-2,3-dimethyl aziridine] tetrafluorobenzene with excess acetic acid at room temperature was followed by titration of the remaining aziridine. The reaction was fairly rapid as evidenced by the disappearance of 70% of the aziridine within six hours. The rate of disappearance of aziridine is shown in Figure 33 and is listed below.

Reaction of Bis-[cis-2,3-dimethyl aziridine]tetrafluorobenzene With Excess Acetic Acid at 23°C

Reaction Time	% Unreacted Aziridine
1	76.7
3	45.9
6	21.3

The half-life of the reaction under these conditions is 2 hours 40 minutes. For comparison, the half-life for the reaction of cis-N-[p-toluenesulfonyl]-2,3-dimethyl aziridine with excess acetic acid at 50°C is 42.5 hours.

FIGURE 33


REACTION OF BIS-[cis-2,3-DIMETHYL AZIRIDINE]TETRAFLUOROBENZENE
WITH EXCESS ACETIC ACID AT 23°C
% UNREACTED AZIRIDINE
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
REACTION TIME, HOURS

F. EVALUATION OF ISOCYANATES

With respect to isocyanate cure systems for OH-terminated binders we have initially taken the position that there is presently no convincing evidence for the need of new isocyanate structures. However, it was felt that two factors required further studies. One factor was the lack of commercially available triisocyanates of acceptable purity. Methods to isolate pure triisocyanates from commercial sources were therefore explored. The second factor arises from the fact that there is a relatively large number of different diisocyanate structures available. The question arises therefore whether there is a preferred diisocyanate structure which will give optimum mechanical properties.

There are basically two types of cure systems for OH-functional prepolymers:

(1) One system employs diisocyanates as chain extenders and triols as crosslinkers;

(2) Another system is based on di/triisocyanates, the triisocyanate functioning as a crosslinker

The di/triisocyanate cure system has potential advantages over the diisocyanate/triol system. In the latter system the diisocyanate may preferentially react with the triol if the hydroxyl groups of the triol are more reactive than those of the prepolymer. As a result, the reaction product of diisocyanate with the triol may separate from the binder matrix. In the di-/triisocyanate system both isocyanates compete with the hydroxyl groups of the prepolymer and no heterogeneous phase can form.

The application of the di-/triisocyanate cure system to hydroxy-terminated prepolymers has been limited by the availability of commercial triisocyantes. The Upjohn Company produces polymethylene polyphenylisocyanate which is marketed under the tradename, PAPI. This material is a dark-colored nonvolatile liquid, which according to the manufacturer is approximately a trifunctional polyisocyanate. Mobay Chemical Company markets triphenyl methane triisocyanate under the tradename, MONDUR TM. It is a brown to brownish purple liquid which is sold as a 20% solution in methylene chloride.

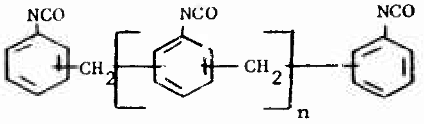
Both of these triisocyanates are quite impure which has limited their application as crosslinking agents for OH-terminated propellant binders. Also because of their impure composition the full potential of the pure triisocyanates has not been adequately assessed.

One of our first objectives has, therefore, been the purification of these polyisocyanates and their evaluation in gumstocks.

1. Purification of Commercially Available Triisocyanates

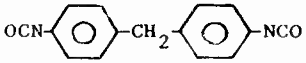
1.1. Isolation of Pure Triphenyl Dimethylene Triisocyanate from PAPI

PAPI is a polyisocyanate which has the theoretical structural formula:



We initially attempted to isolate the pure triisocyanat[illegible] um distillation. At a temperature of about 150°C and <0.. [illegible] isolated a fraction which accounted for about 50% of the total m[illegible] This fraction is a light yellow solid melting at about 40°C. [illegible] uent analysis showed that it was the diisocyanate.

Analysis of the 50% Fraction Isolated by Vacuum Distillation



	Theory	Found
$\overline{M}n$	250	256
Equivalent Weight	125	124.9

A comparison of the infrared spectrum of the distilled fraction, diphenyl methane diisocyante, (see Figure 35) with that of the total polyisocyanate (Figure 36) shows that the distilled product has no carbonyl absorption bands.

Attempts to separate the triisocyanate by vacuum distillation at a higher temperature yielded only a very small fraction of the triisocyanate. At the temperature required (≈250°C) to distill the triisocyanate, decomposition and polymerization prevented the isolation of significant quantities of the triisocyanate. Since the "as received" polyisocyanate is essentially trifunctional, the PAPI apparently is a complex mixture of di-, tri- and polyisocyanates as well as highly colored polymeric components.

Subsequent studies to isolate the triisocyanate by sublimation yielded the following approximate composition of the PAPI mixture:

Diisocyanate	=	49%
Triisocyanate	=	22%
Residue (Polyfunctional)	=	29%

Separation of the triisocyanate by sublimation is not a practical method which can be readily scaled-up. We have therefore developed a two-step technique which involves (1) separation of the undesirable, highly colored components by precipitation, and (2) subsequent vacuum distillation of the filtrate to isolate pure di- and triisocyanate.

The specific procedure which we currently use is as follows:

- 300 g of PAPI is dissolved in 500 ml of carbon tetrachloride
- 750 ml of n-pentane is added to the solution. The dark-brown precipitate that settles out is removed by filtration and discarded.
- The filtrate is then stripped free of solvent
- The di- and triisoycanate are subsequently isolated by vacuum (~0.1 mm Hg) distillation at about 150°C and 250°C respectively.

The distilled triphenyl dimethylene triisocyanate is a white to pale yellow solid which melts at about 70°C. The yield of triisocyanate based on total PAPI is about 10-15%. The infrared spectrum of purified triphenyl dimethylene triisocyanate is shown in Figure 36.

Analysis of the triphenyl dimethylene triisocyanate gave the following results:

	Theory	Found
Mn	381	372,378
Equivalent Weight	127	126.8

1.2. Isolation of Pure Triphenyl Methane Triisocyanate from MONDUR TM

The isolation of pure triphenyl dimethylene triisocyanate from the commercially available "PAPI"-mixture prompted studies to purify another available triisocyanate.

Mobay sells triphenyl methane triisocyanate under the trade name, MONDUR TM. The material as supplied by Mobay is a brown to brownish-purple liquid containing 20% solids in methylene chloride. In its commercially available form this triisocyanate has a number of disadvantages:

- The material must be stored in solution. When stored neat it will readily homopolymerize at room temperature to form an insoluble solid.

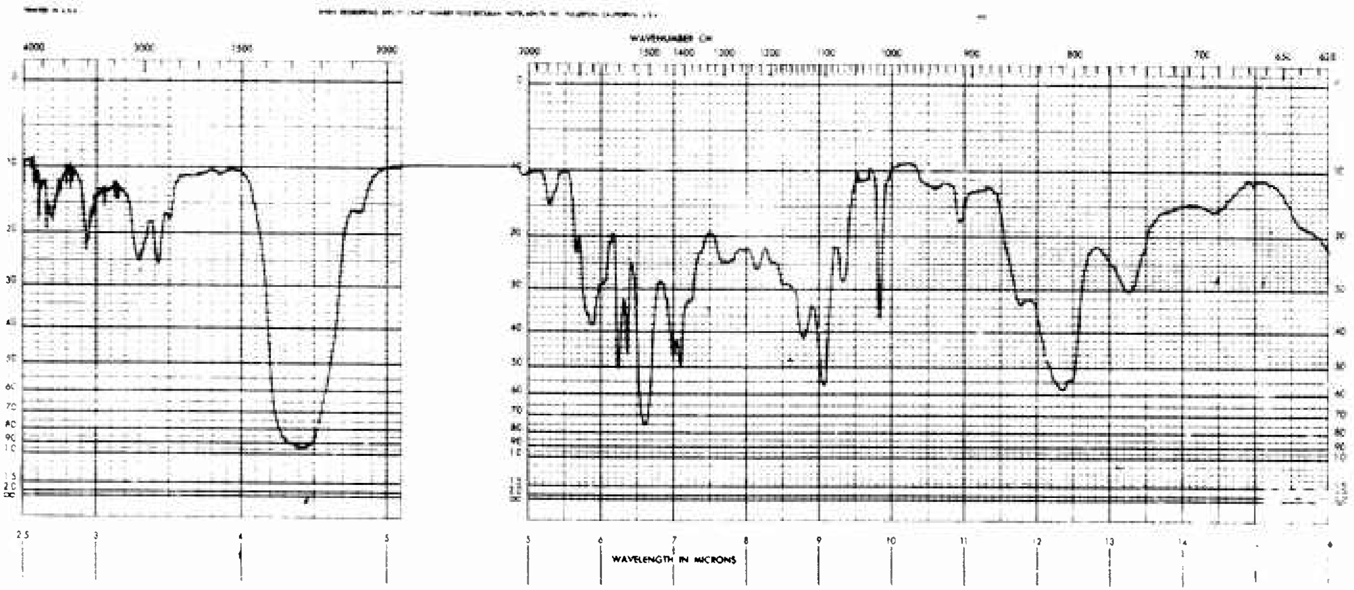


Figure 34. Infrared spectrum of polymethylene polyphenylisocyanate (PAPI) as received, capillary layer between NaCl plates.

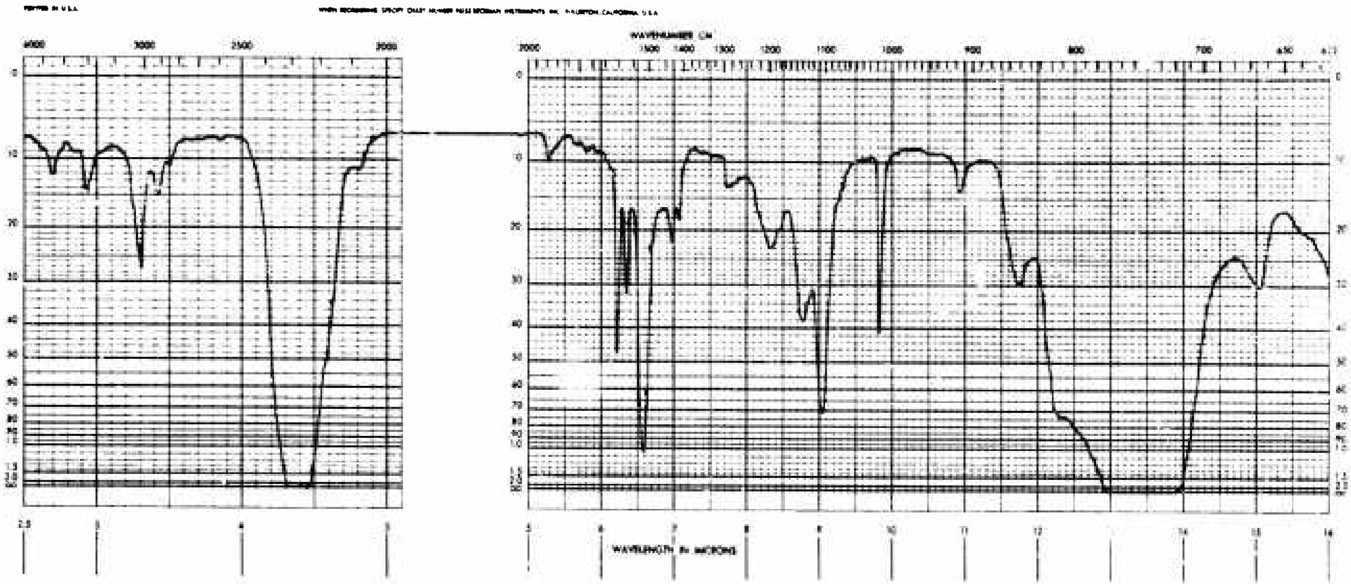


Figure 35. Infrared spectrum of a polyphenylisocyanate fraction (Mn=256) isolated by distillation under vacuum in chloroform solution using matched cells. This fraction is diphenyl methane diisocyanate.

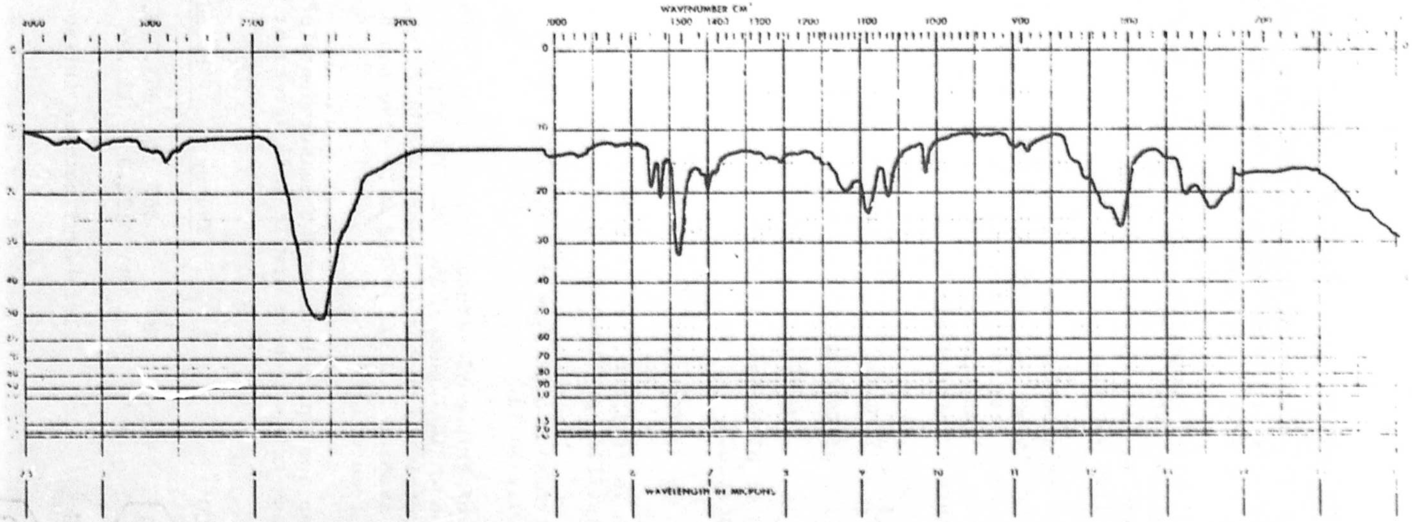


Figure 36. Infrared spectrum of purified triphenyl dimethylene triisocyanate, capillary layer between NaCl plates.

- Use of MONDUR TM as a curing agent for OH-terminated propellant binders requires removal of the methylene chloride solvent from the propellant mix.

- It is quite impure, containing components having less than trifunctionality. MONDUR TM also contains hydrolyzable chloride which may affect the stability of propellants cured with this triisocyanate.

We have purified triphenylmethane triisocyanate by a method similar to the one employed to isolate pure triphenyl dimethylene triisocyanate. The technique presently used consists of (1) precipitating undesirable components by the addition of n-pentane to MONDUR TM and (2) subsequently isolating pure triisocyanate by vacuum distillation.

Specific conditions are as follows:

- Add 150 ml of n-pentane to 100 g of MONDUR TM Solution (20% TTI)

- A dark brown to black precipitate settles out immediately which is discarded.

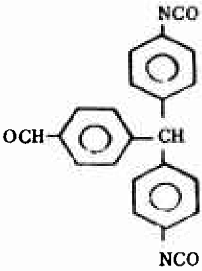
- The solution is filtered.

- The filtrate is stripped free of solvent and the residue is vacuum distilled at about 230°C and 250μ pressure.

The distilled triisocyanate (yield about 50%) crystallizes slowly to an off-white waxy solid.

The IR spectra of triphenyl methane triisocyanate before and after purification are shown in Figure 37 and 38. The impure triphenyl methane triisocyanate contains a number of absorbance bands which are not present in the purified sample: 5.83μ, 5.92μ. Also the band at 7.14μ has been greatly reduced.

Molecular weight and equivalent weight measurements of the purified triphenyl methane triisocyanate are in good agreement with theory.



	Theory	Found
Mn	367	365,378,368
Eq. Wt.	122.3	121.9

Triphenyl methane triisocyanate

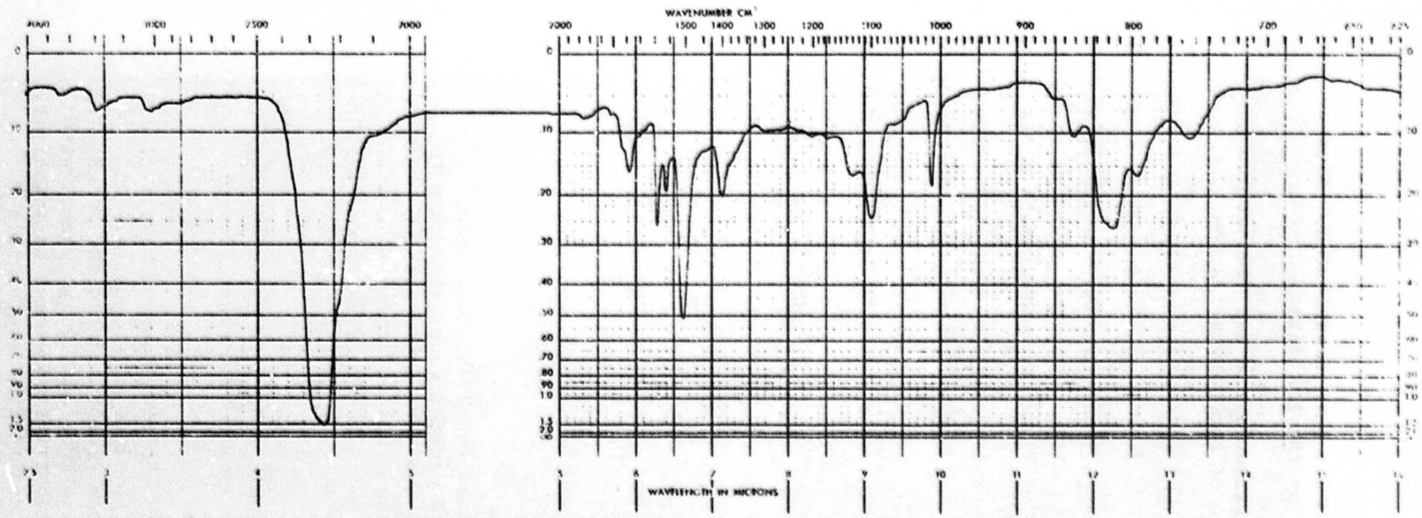


Figure 37. IR spectrum of triphenylmethane triisocyanate (Mondur TM) as received (solvent free).

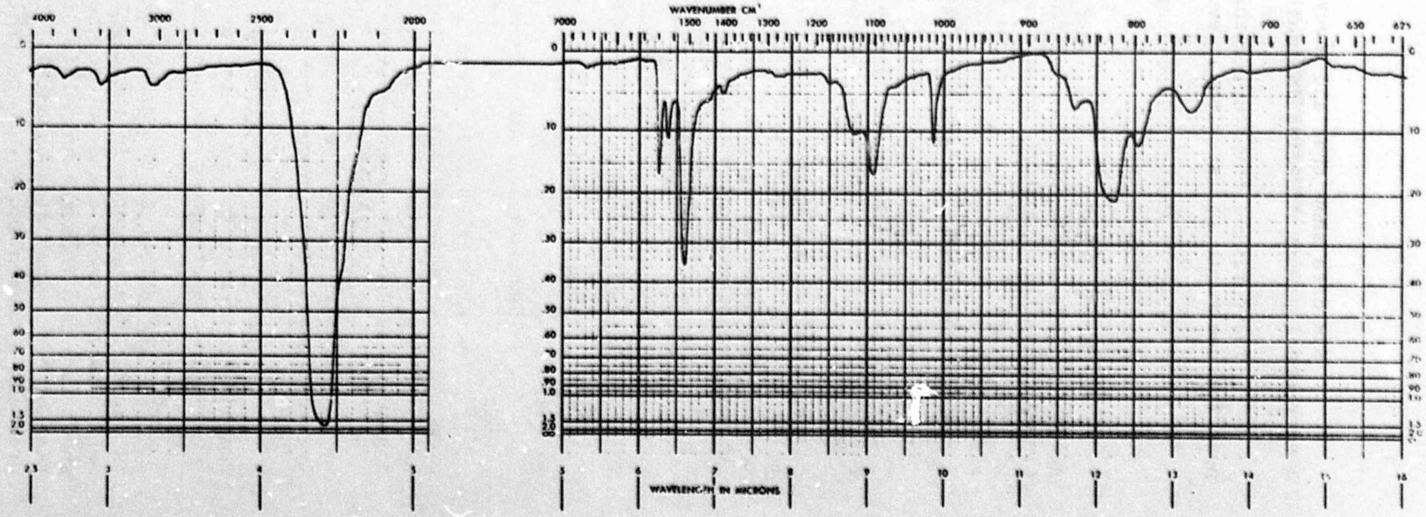


Figure 38. IR spectrum of purified triphenyl methane triisocyanate.

NMR data show that all isocyanates are para substituted. Also a very small amount of amine is indicated by the NMR data.

The purified triphenyl methane triisocyanate has been stored neat for one month so far without evidence of homopolymerization.

2. Kinetic Studies of Isocyanates with OH-Telagen-S

The OH-Telagen-S prepolymer has reportedly secondary hydroxyl groups to reduce its reactivity with isocyanates. We have carried out kinetic studies at ambient temperature to determine the reactivity of this prepolymer with a number of different diisocyanates and triisocyanates. The results of these studies are discussed in the following sections. All rate studies were carried out at a NCO/OH=1.0.

2.1. Reactivity of OH-Telagen-S with Different Diisocyanates

Reaction profiles of OH-Telagen-S with the following four diisocyanates were determined at room temperature by infrared measurements of the isocyanate absorption band at 4.4μ using the 3.4μ band as an internal reference.

- Diphenyl methane diisocyanate
- 2,4-Tolylene diisocyanate
- Bitolylene diisocyanate
- Hexamethylene diisocyanate

As expected and as shown in Figures 39 and 40 , the three aromatic diisocyanates showed considerably greater reactivity than the aliphatic diisocyanate. Out of the three aromatic diisocyanates, the diphenyl methane diisocyanate exhibited the greatest reactivity with a half-life of one hour. In the case of the diphenyl methane diisocyanate, both isocyanate groups are believed to have equal reactivity with the hydroxyl group of the prepolymer.

The 2,4-tolylene diisocyanate showed reduced reactivity after the 50% conversion point. This reflects the different reactivity of the two isocyanate groups on the ring.

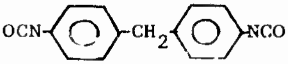
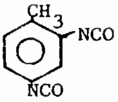
The effect of CH_3-groups ortho to the NCO group on reactivity is clearly demonstrated in the case of bitolylene diisocyanate. The methyl substituents ortho to the isocyanate groups reduced the reactivity about ten-fold (compare half-life of diphenyl methane diisocyanate with that of bitolylene diisocyanate). This substitution effect on reactivity provides a convenient key to control the reactivity of aromatic isocyanates.

The hexamethylene diisocyanate chain extender exhibiting a half-life of about 30 hours showed considerably lower reactivity than the aromatic diisocyanates. This is also reflected by practical experience which shows that aliphatic diisocyanates provide longer pot-life than aromatic diisocyanates.

The 50% conversion points for the four different diisocyanates are summarized in Table IIL.

TABLE IIL

COMPARISON OF REACTIVITY OF DIFFERENT DIISOCYANATE STRUCTURES WITH OH-TELAGEN-S AT AMBIENT TEMPERATURE

Diisocyanate	Structure	t (1/2) (50% Conversion) (Hours)
diphenyl methane diisocyanate		1
2,4-Tolylene diisocyanate		6
Bitolylene diisocyanate		9
Hexamethylene diisocyanate	$OCN(CH_2)_6NCO$	30

From the standpoint of pot-life aliphatic diisocyanates are preferred. However, in a di-/triisocyanate cure system employing an aromatic triisocyanate, the reactivity of the diisocyanate should be approximately matched to the reactivity of the triisocyanate. An aromatic triisocyanate such as triphenyl dimethylene triisocyanate matches the reactivity of aromatic diisocyanates more closely than an aliphatic diisocyanate, such as hexamethylene diisocyanate.

Our gumstock studies have also shown (see Section F-3) that aromatic diisocyanates result in higher maximum tensile strength than hexamethylene diisocyanate at comparable maximum strain levels.

Aromatic diisocyanates are therefore preferred because of improved mechanical properties whereas aliphatic diisocyanates would give extended pot lifes. It appears that an optimum cure system will be a compromise between optimum processing life, reasonable cure rate and optimum mechanical properties.

FIGURE 39

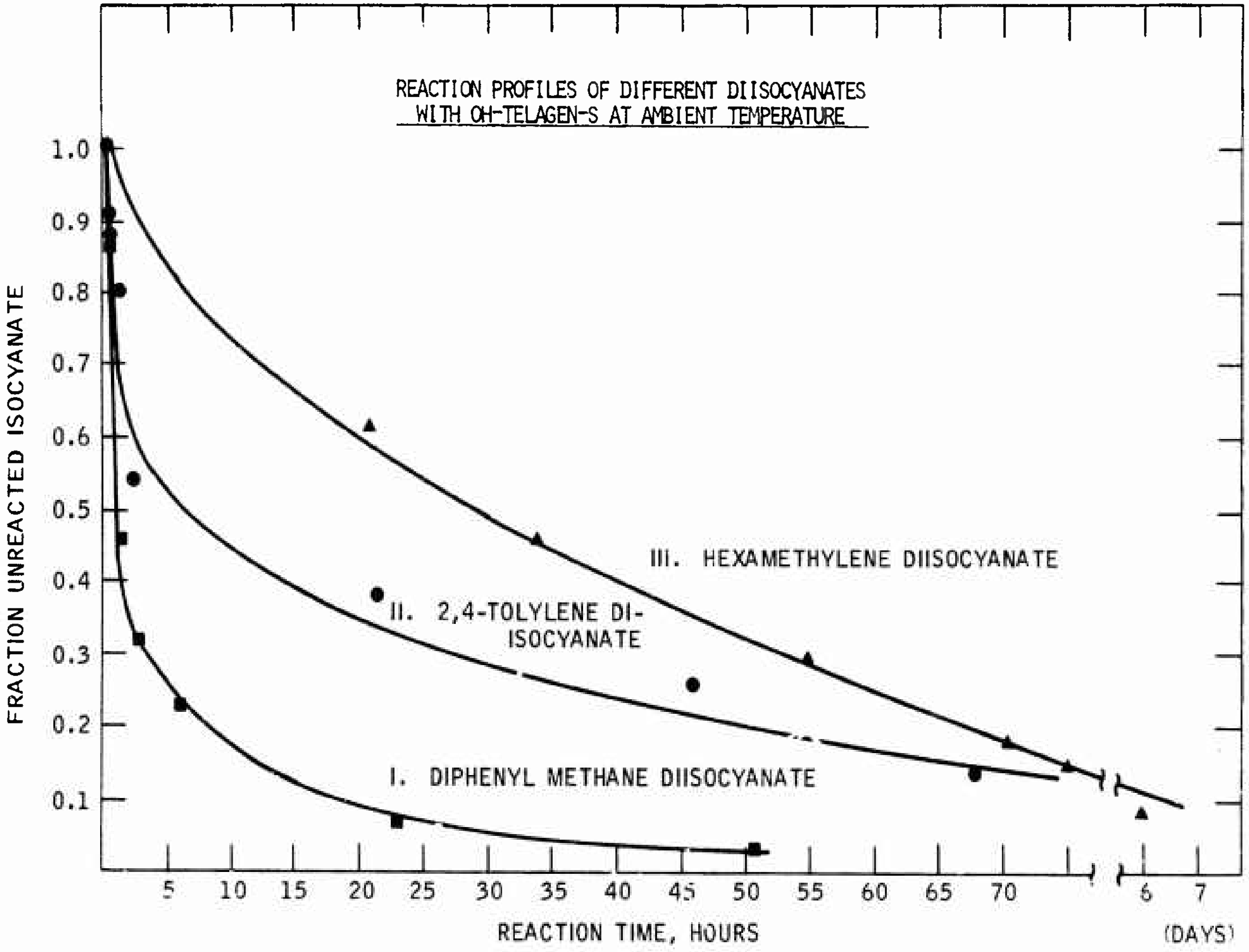
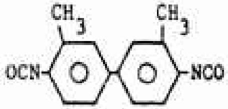
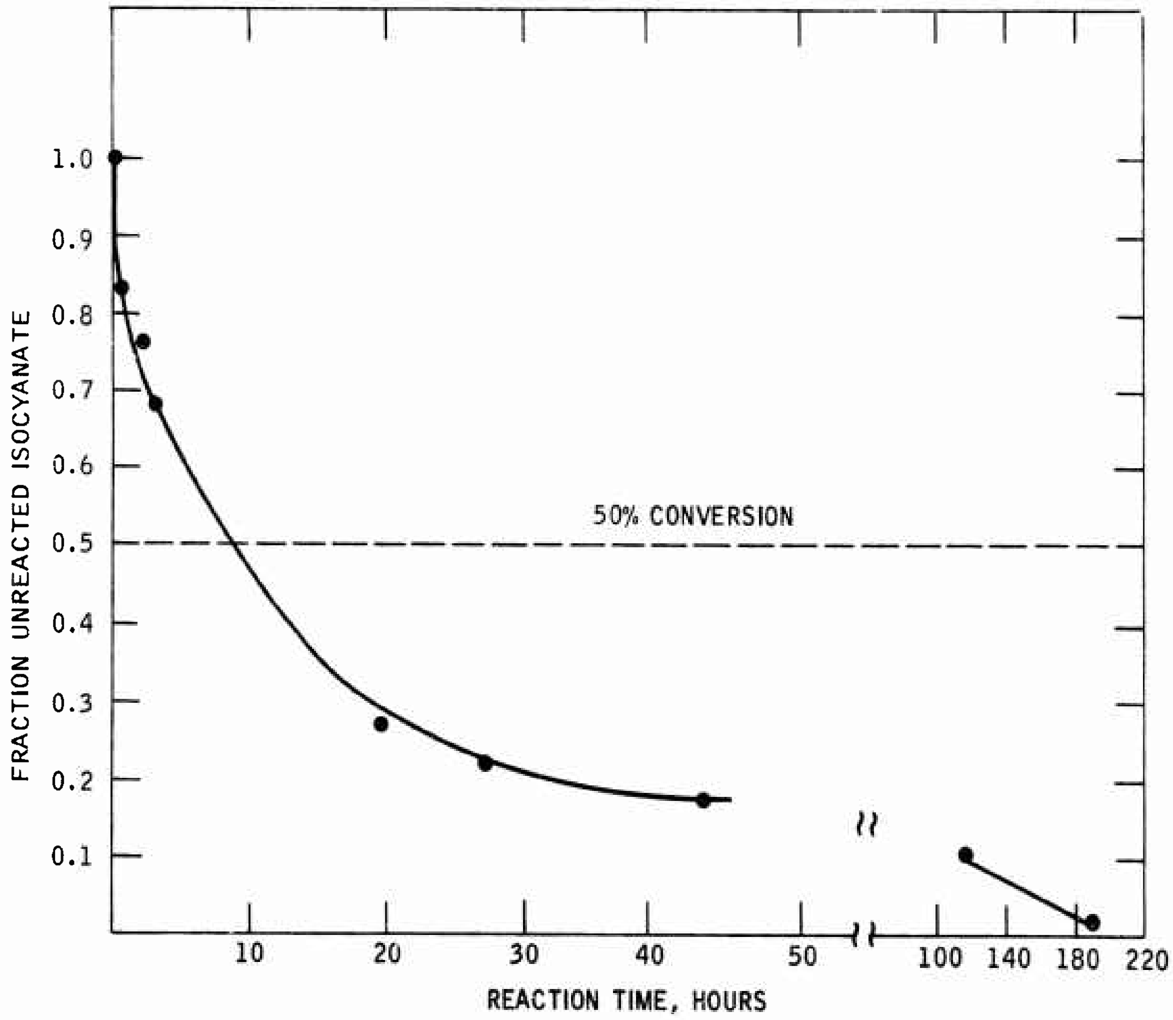

REACTION PROFILES OF DIFFERENT DIISOCYANATES WITH OH-TELAGEN-S AT AMBIENT TEMPERATURE

Figure 40. Reaction profile of OH-Telagen-S with bitolylene diisocyanate, at room temperature. Rate was monitored by infrared.





2.2. Reactivity of OH-Telagen-S with Triisocyanates

The successful purification of triphenyl dimethylene triisocyanate and triphenyl methane triisocyanate prompted a study of the reactivity of these triisocyanates with OH-Telagen-S.

a. Reactivity with Triphenyl Dimethylene Triisocyanate

To determine the true reactivity of the triphenyl dimethylene triisocyanate with the OH-Telagen-S prepolymer the triisocyanate was first dissolved in di-octyl phthalate plasticizer and the solution subsequently added to the prepolymer. The prepolymer thus contained 5% di-octyl phthalate plasticizer. The resulting reaction profile at ambient temperature is shown in Figure 41. The 50% conversion point is about one hour which is equal to that of the diphenyl methane diisocyanate. The reactivity of the triphenyl dimethylene triisocyanate is therefore most closely matched by the corresponding diisocyanate.

The reaction profile of OH-Telagen-S with an 8/2 equivalent mixture of diphenyl methane diisocyanate/triphenyl dimethylene triisocyanate is shown in Figure 42. Since the di- and triisocyanate have about equal reactivity the reaction profile of the mixture is very similar to that of the individual components.

b. Reactivity with Triphenyl Methane Triisocyanate

The reaction profile of the purified triphenyl methane triisocyanate with secondary OH-Telagen-S, at ambient temperature is presented in Figure 43. This triisocyanate was added in the liquid state and no plasticizer was used. As previously stated, the reaction was monitored by infrared absorption measurements by following the disappearance of the isocyanate band at 4.4µ. The reactivity of this triisocyanate is high, the half life (t 1/2) being less than 30 minutes.

Reactivity of Triisocyanates With OH-Telagen-S at Ambient Temperature

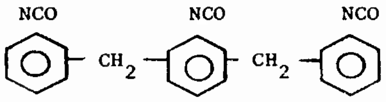
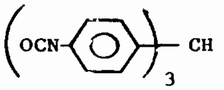
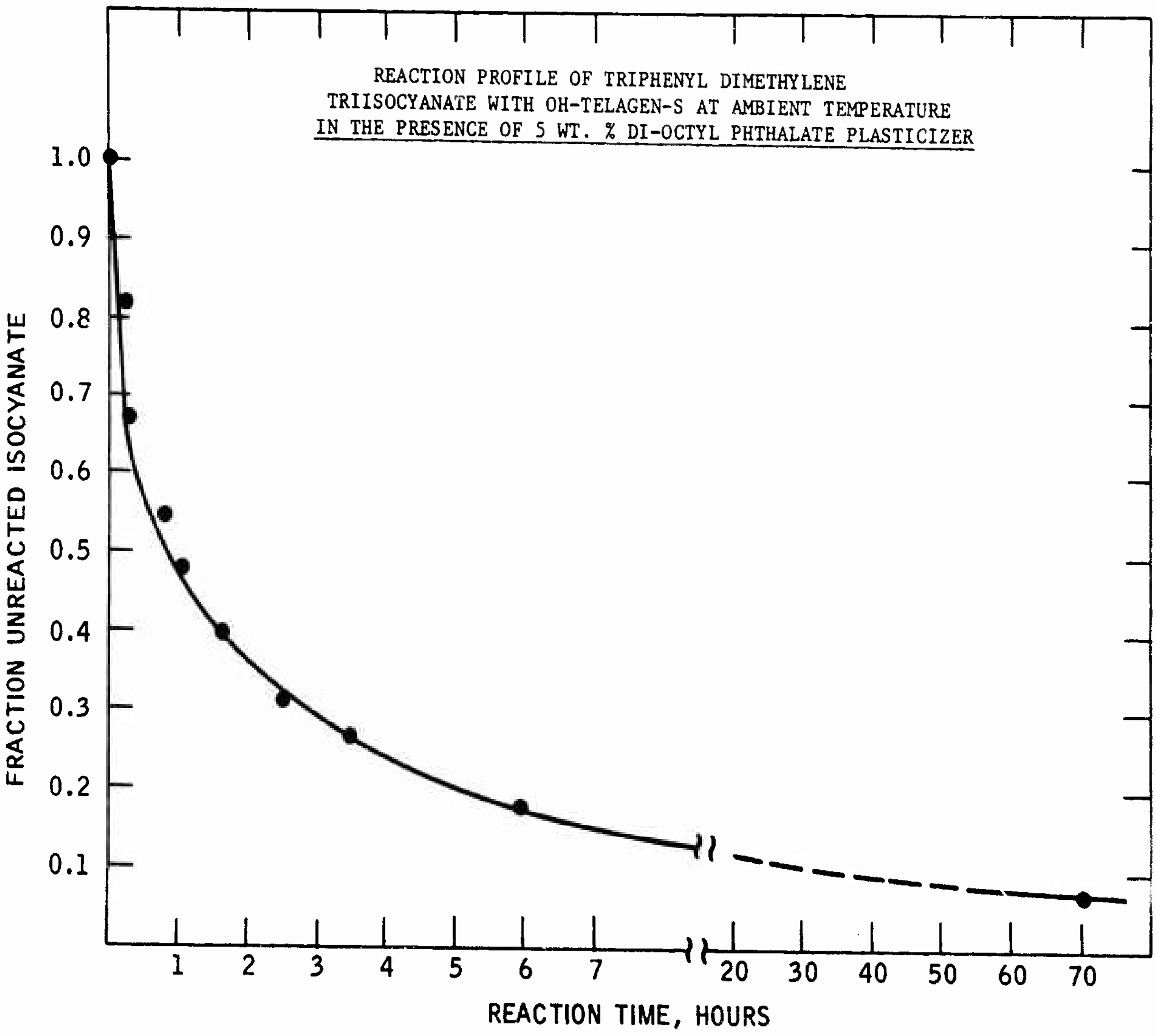
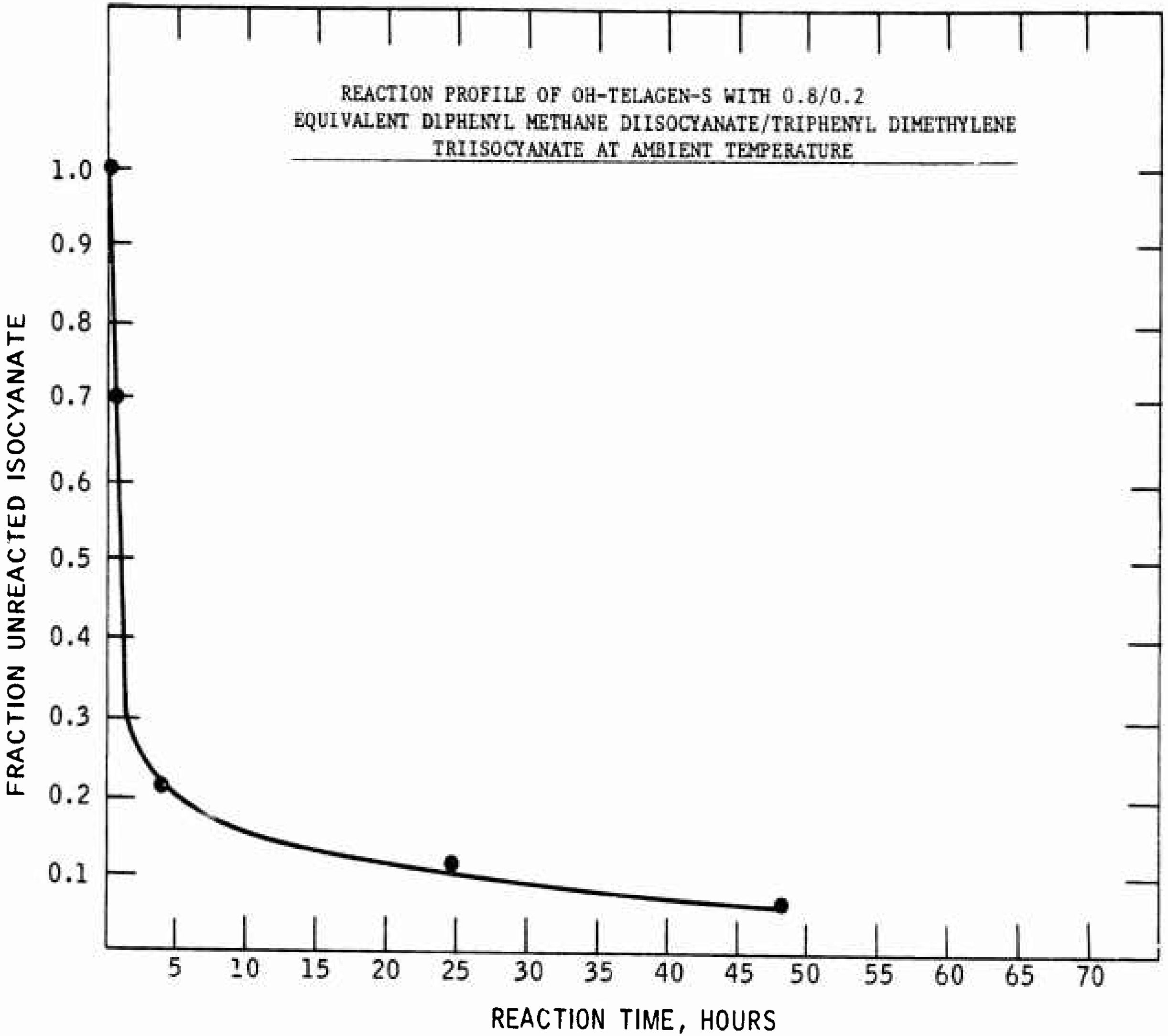
Triisocyanate	Structure	t (1/2) (50% Conversion)
Triphenyl dimethylene triisocyanate		1 hour
Triphenyl methane triisocyanate		<30 minutes

FIGURE 41



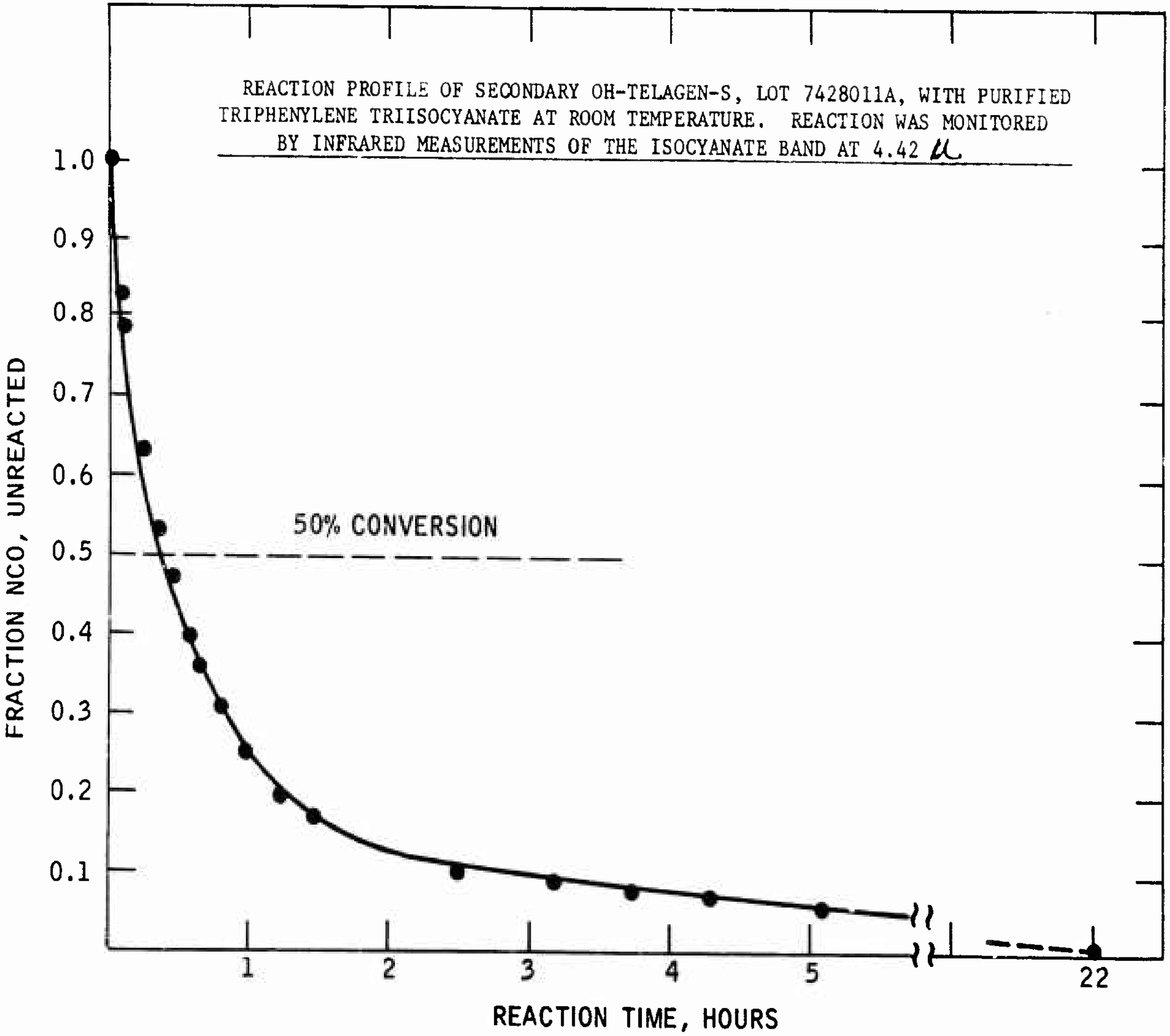
REACTION PROFILE OF TRIPHENYL DIMETHYLENE TRIISOCYANATE WITH OH-TELAGEN-S AT AMBIENT TEMPERATURE IN THE PRESENCE OF 5 WT. % DI-OCTYL PHTHALATE PLASTICIZER

FIGURE 42



REACTION PROFILE OF OH-TELAGEN-S WITH 0.8/0.2 EQUIVALENT DIPHENYL METHANE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE AT AMBIENT TEMPERATURE

FIGURE 43



REACTION PROFILE OF SECONDARY OH-TELAGEN-S, LOT 7428011A, WITH PURIFIED TRIPHENYLENE TRIISOCYANATE AT ROOM TEMPERATURE. REACTION WAS MONITORED BY INFRARED MEASUREMENTS OF THE ISOCYANATE BAND AT 4.42 μ

3. Mechanical Properties of OH-Telagen-S Gumstocks Cured with Mixtures of Di-/Triisocyanates

The use of di/triisocyanates as curatives for hydroxy-terminated prepolymers has not been adequately explored because of the lack of commercially available triisocyanates of acceptable purity. The isolation of two pure triisocyanates on this program has prompted an investigation of di/triisocyanate cure systems in an OH-Telagen-S gumstock. Since there is a great number of different diisocyanate structure available, the question arises whether there is a preferred diisocyanate structure which will give optimum stress and strain levels. Before we can design new improved diisocyanates, therefore, we must determine what the effect of diisocyanate structures is, if any, on the mechanical properties of cured gumstocks before and after heat aging. We have therefore carried out gumstock studies to evaluate the effect of diisocyanate structure and di-/triisocyanate ratio on such mechanical properties as maximum stress, strain at break, initial modulus and hardness. Mechanical property measurements were made on unaged gumstocks as well as gumstocks aged at 275°F in a nitrogen atmosphere.

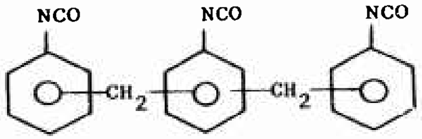
3.1. Effect of Di-/Triisocyanate Ratio and Diisocyanate Structure on Mechanical Properties of: Unaged Gumstocks at Ambient Temperature and at 180°F

The prepolymer used in these studies was a sample of the hydrogenated polybutadiene prepolymer, OH-Telagen-S, lot 7428011A, which had been supplied by Lockheed. This polymer has a nominal molecular weight of 2000.

All mechanical property measurements were made with micro-dumbbells at a crosshead speed of 2 inches/minute. All data reported in this section are based on 5 individual measurements.

Gumstocks were cured at 150°F for 6 days.

All gumstocks were cured with mixtures of di- and triisocyanates. Triphenyl dimethylene triisocyanate,



, was used as the crosslinker. The NCO/OH ratio was kept constant at 1/1. The following variables were investigated:

(1) di-/triisocyanate ratio from 9/1 to 100% triisocyanate and

(2) four different diisocyanate structures.

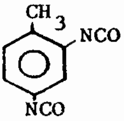
The four diisocyanate structures included one aliphatic and three aromatic diisocyanates. These are the same diisocyanates for which kinetic data had been obtained.

The four diisocyanates represent the following structural features:

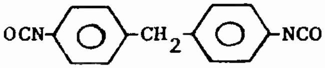
1. HDI, Hexamethylene diisocyanate; $(OCN(CH_2)_6NCO)$; This diisocyanate was chosen to represent an aliphatic diisocyanate structure.

The three aromatic diisocyanates represent the following structural differences:

2. TDI, Tolylene diisocyanate; both isocyanate groups are attached to the same phenyl ring.



3. DPMD, Diphenyl methane diisocyanate; each isocyanate group is attached to a separate phenyl ring and the two phenyl rings are linked by a methyl group.



4. BTD, Bitolylene diisocyanate; each isocyanate group is again attached to a separate phenyl ring. Both isocyanate groups are shielded by a methyl group ortho to the isocyanate. Also the two phenyl rings are directly linked (biphenyl) to provide a less flexible chain.

The stress-strain data were measured at a crosshead speed of 2 in/minute. Mechanical properties at ambient temperature for the four cure systems are summarized in Tables IL through LVI and graphically represented in Figures 44 through 51.

On the basis of these data, we offer the following tentative conclusions:

Maximum Strain at Ambient Temperature (Figures 44 and 45)

- As expected the % strain at maximum stress (equal to maximum strain) decreases sharply with increase in triisocyanate level (increase in crosslink density) reaching a minimum at the 100% triisocyanate level. The decrease in strain level is most severe at triisocyanate equivalent levels from 0-50% (see Figure 44).

- Most significantly the maximum strain level is primarily determined by the triisocyanate level. Differences in the structure of diisocyanates have only secondary effects on the maximum strain level.

- Figure 45 graphically illustrates the dependence of the percent strain at maximum stress on triisocyanate level using two different triisocyanates. The individual data points are those obtained using triphenyl methane triisocyanate as crosslinker and diphenyl methane diisocyanate as chain extender. The solid line represents the average measurement obtained when using triphenyl dimethylene triisoycanate as crosslinker and four different diisocyanates as chain extenders (line from Figure 44). The data show that differences in the structure of these triisocyanates have no significant effect on the percent strain at maximum stress.

- From the standpoint of optimizing the maximum strain level there is apparently no preferred diisocyanate structure. The strain level is solely dependent on the triisocyanate level.

Maximum Strain at 180°F (Figure 46)

- As expected the strain at maximum stress was significantly reduced at 180°F for each comparable di-/triisocyanate ratio.

- Figure 46 allows a comparison of the % strain at maximum stress at ambient temperature and at 180°F. At the higher temperature (180°F) the maximum strain is reduced, resulting in a lower but similar curve as compared to the ambient temperature dependence of maximum strain on triisocyanate level.

- As noted before at ambient temperature measurements, the maximum strain level is primarily determined by the triisocyalate level. Differences in the structures of the diisocyanate have only secondary effects on the maximum strain level. This applies also at 180°F.

FIGURE 44

DEPENDENCE OF STRAIN AT MAXIMUM STRESS
ON TRIISOCYANATE LEVEL AT AMBIENT TEMPERATURE

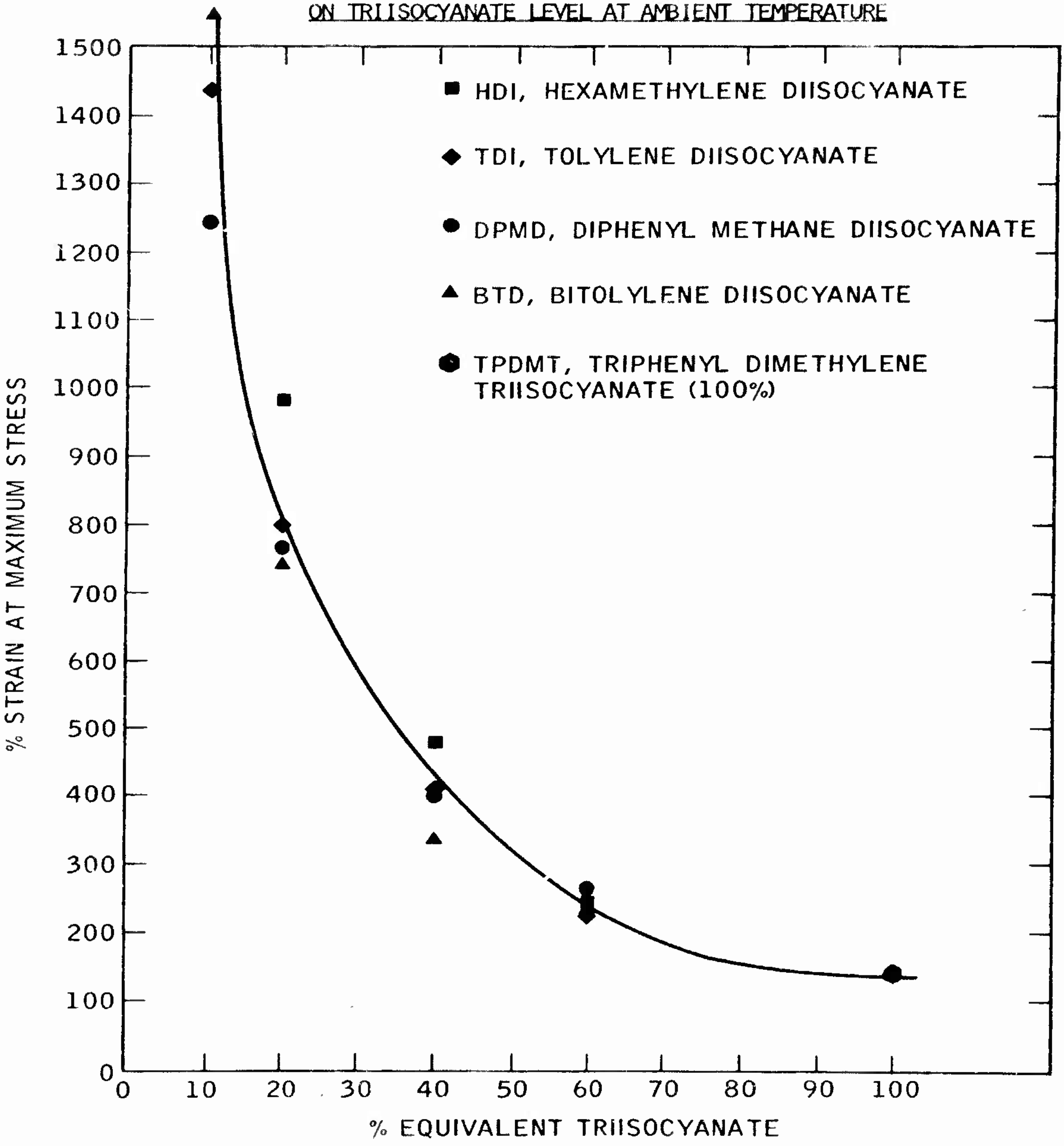


FIGURE 45

DEPENDENCE OF % STRAIN AT MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT AMBIENT TEMPERATURE

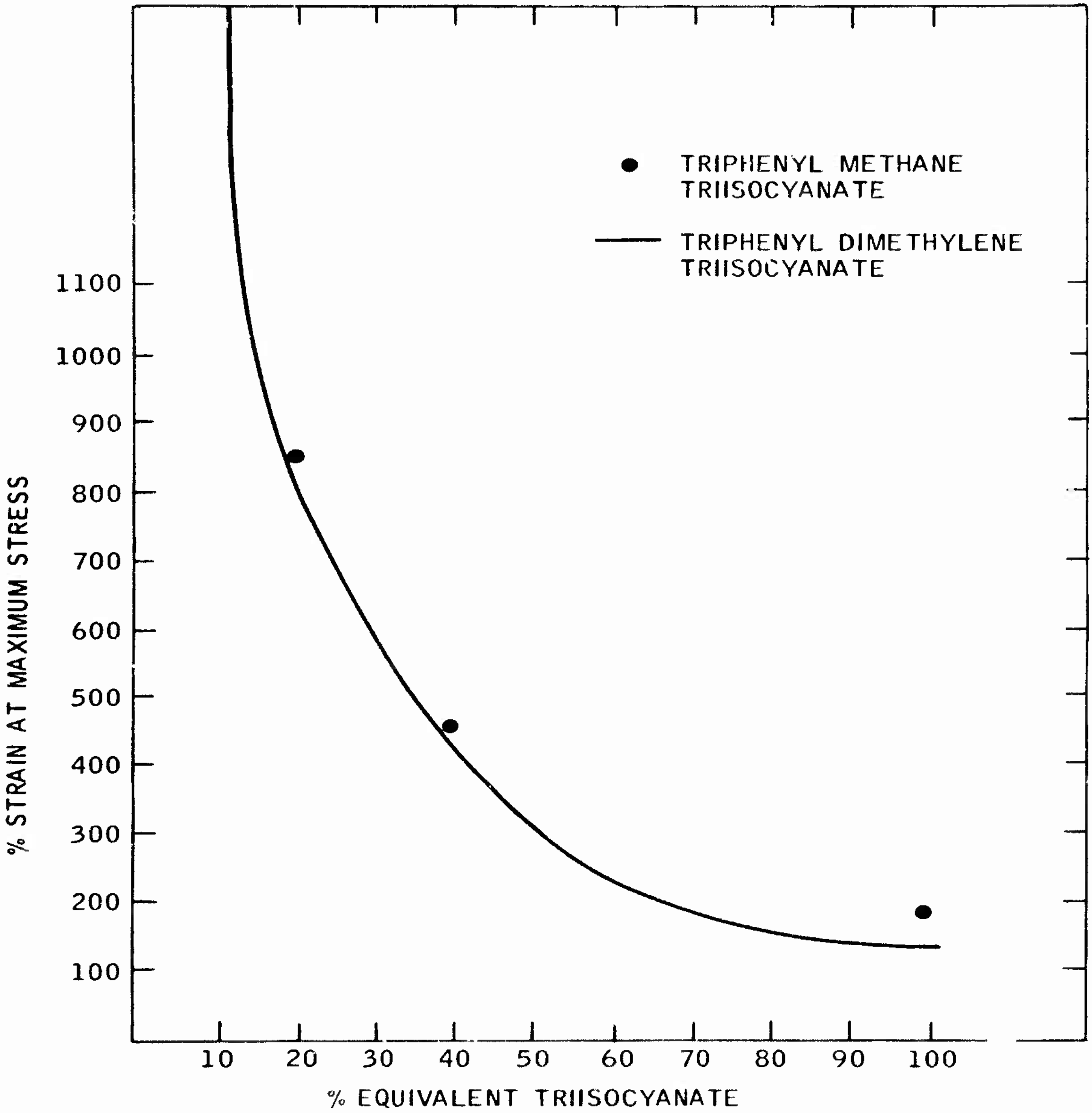
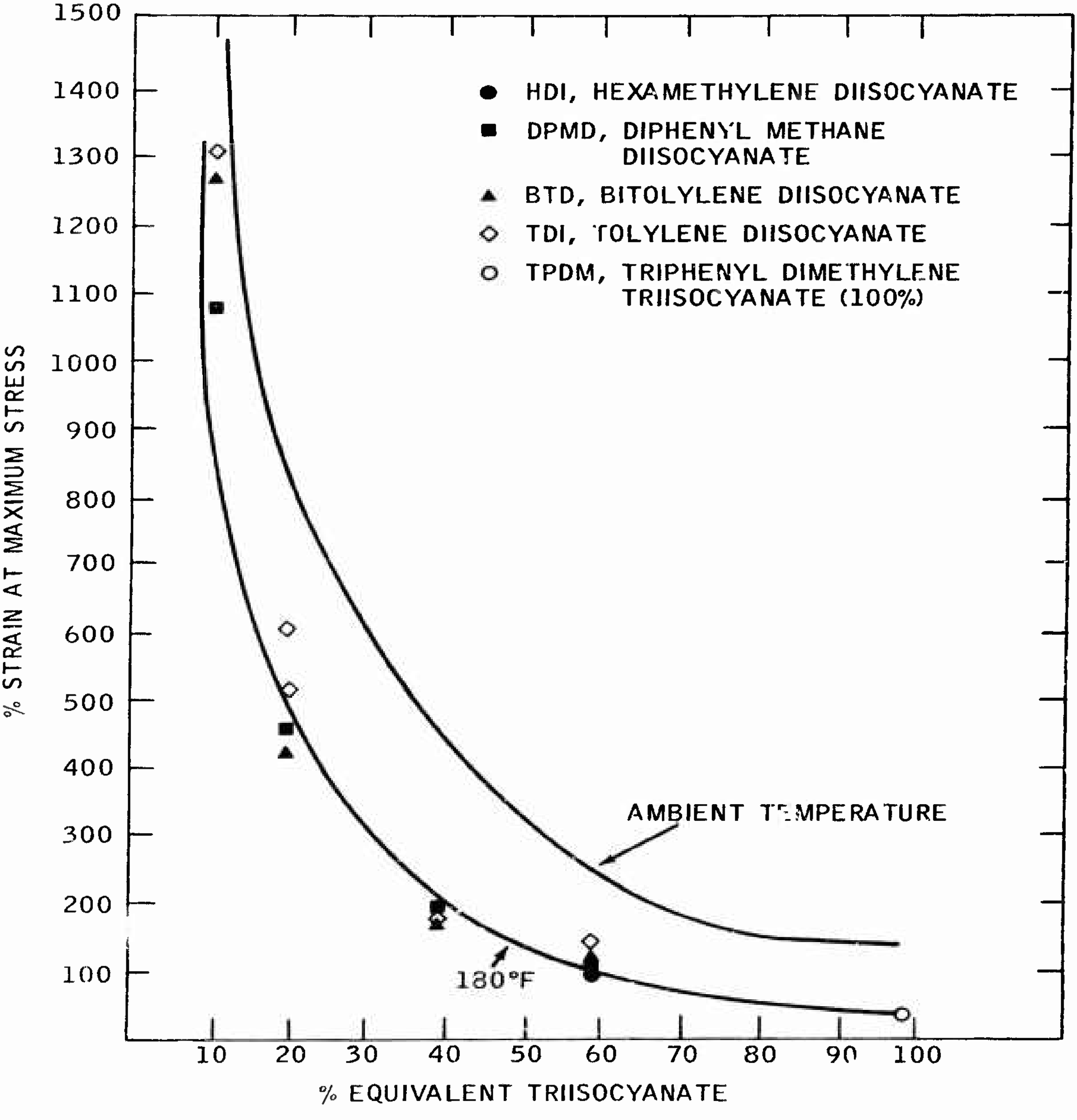


FIGURE 46

DEPENDENCE OF % STRAIN AT MAXIMUM STRESS ON TRIISOCYANATE LEVEL USING FOUR DIFFERENT DIISOCYANATE CHAIN EXTENDERS

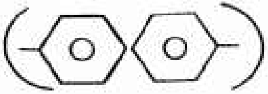
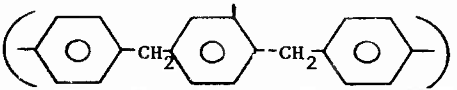


Maximum Stress at Ambient Temperature (Figure 47)

- The maximum stress (also equal to the stress at break) shows a dual dependence on (a) triisocyanate level and (b) structure of the diisocyanate.

- For both hexamethylene diisocyanate and tolylene diisocyanate chain-extended gumstocks, the maximum stress level increases with increase in triisocyanate level. Tolylene diisocyanate reaches the maximum stress level at about 40 equivalent % of triisocyanate whereas the aliphatic diisocyanate, HDI, requires a triisocyanate level in excess of 60% to reach maximum stress.

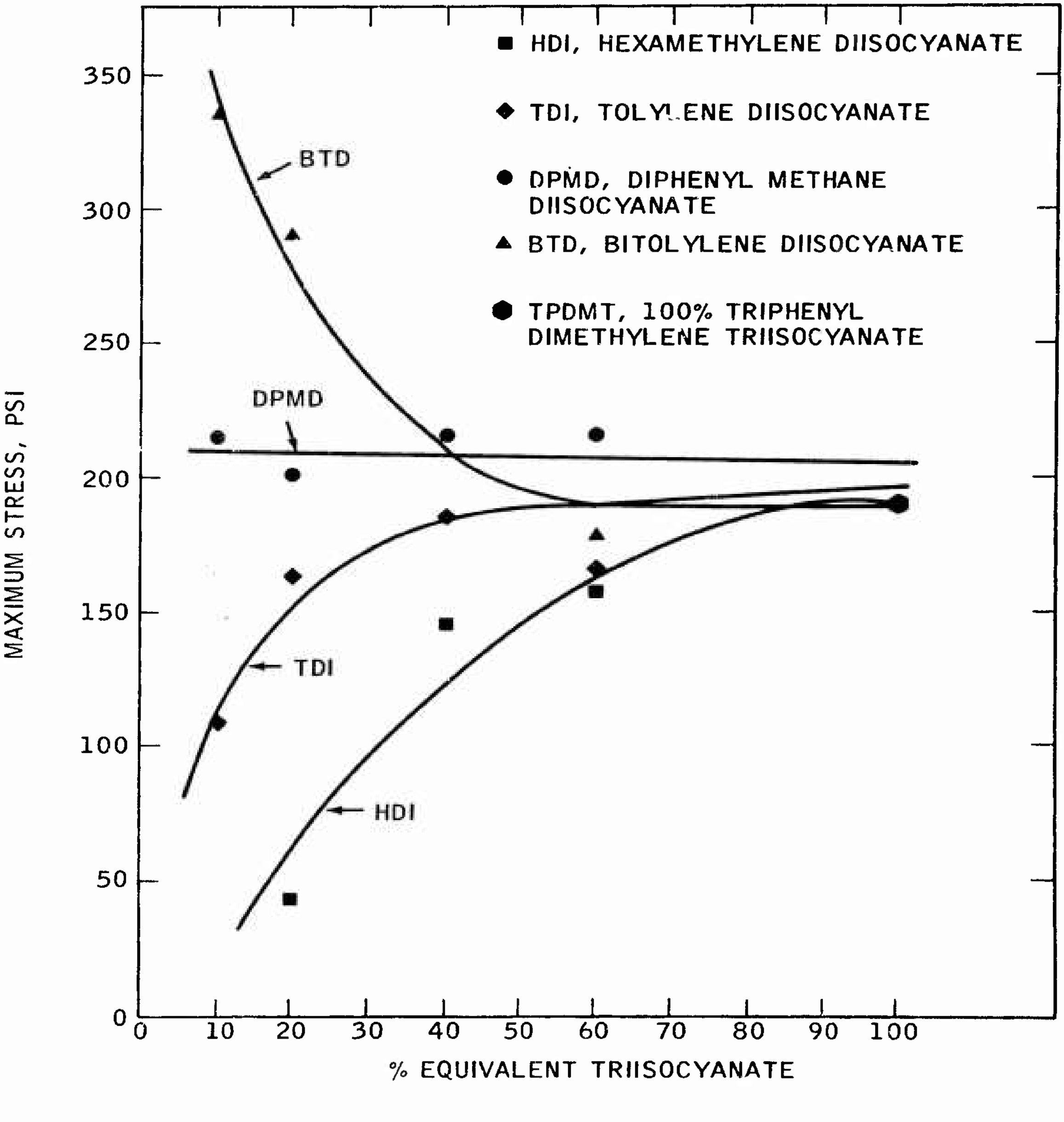
- Gumstocks chain extended with diphenyl methane diisocyanate show an independence of maximum stress level with triisocyanate concentration. It should be remembered in this connection that the diphenyl methane diisocyanate has the same backbone structure as the triphenyl dimethylene triisocyanate. One possible explanation for this concentration independence of maximum stress with triisocyanate level is this identity in backbone structure. Another plausible explanation is that the difunctional curative acts in fact as a trifunctional crosslinker through an ionic mechanism of the urethane cure-linkage.

- Bitolylene diisocyanate shows a very unique behavior. The maximum stress decreases with increase in triisocyanate level, reaching a plateau at the 40-60% triisocyanate level. The fact that maximum stress increased with increase in diisocyanate content must again reflect the structural behavior of this particular diisocyanate. Bitolylene diisocyanate contains the very rigid biphenyl linkage  which apparently dictates the maximum stress level. The triisocyanate, , contains CH_2 links between the phenyl rings and thereby modifies the rigidity of the backbone.

This strong dependence of maximum stress on diisocyanate structure implies that there is an optimum diisocyanate structure which should combine optimum tensile strength with optimum strain capability. Bitolylene diisocyanate seems to fit this criterion best. However, as subsequently discussed the bitolylene diisocyanate also exhibits the maximum initial modulus at the high diisocyanate level which seriously detracts from the combined advantage of high stress and strain when using this diisocyanate.

FIGURE 47

DEPENDENCE OF MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT AMBIENT TEMPERATURE



Maximum Stress at 180°F (Figure 48)

Figure 48 shows the dependence of maximum stress at 180°F on triisocyanate level and diisocyanate structure. The data clearly show that:

- There is a significant reduction in stress level at 180°F as compared to ambient temperature at every comparable triisocyanate level.
- Aromatic diisocyanates result in higher maximum stress levels than the aliphatic diisocyanate at comparable triisocyanate levels.
- There is no significant difference in stress level between the three aromatic diisocyanate structures. This is in contrast to measurements at ambient temperature where there is a definite effect of aromatic diisocyanate structure on stress level. The observed strong dependence of aromatic diisocyanate structure on maximum stress at ambient temperature must therefore be due to secondary effects: differences in the degree of entanglement, association between curelinkages or hydrogen bonding. At the elevated temperature (180°F) these secondary effects are negated.

Initial Modulus at Ambient Temperature (Figure 49)

- The initial modulus shows an almost linear increase with increase in triisocyanate level for three of the four diisocyanates (HDI, TDI, and DPMD). The bitolylene diisocyanate again occupies a unique position showing a maximum initial modulus at the high diisocyanate content. As pointed out before, this high initial modulus is very undesirable for propellant applications.

Initial Modulus at 180°F (Figure 50)

Figure 50 illustrates the dependence of initial modulus on triisocyanate level at 180°F.

- The initial modulus shows a very steep increase with increase in triisocyanate level.
- Although the aliphatic diisocyanate results in the lowest initial modulus at comparable triisocyanate levels the spread between the four diisocyanate structures is not very pronounced. The effect of diisocyanate structure on initial modulus has been greatly reduced at the elevated temperature (180°F).

FIGURE 48

DEPENDENCE OF MAXIMUM STRESS ON TRIISOCYANATE LEVEL AT 180°F USING FOUR DIFFERENT DIISOCYANATE CHAIN EXTENDERS

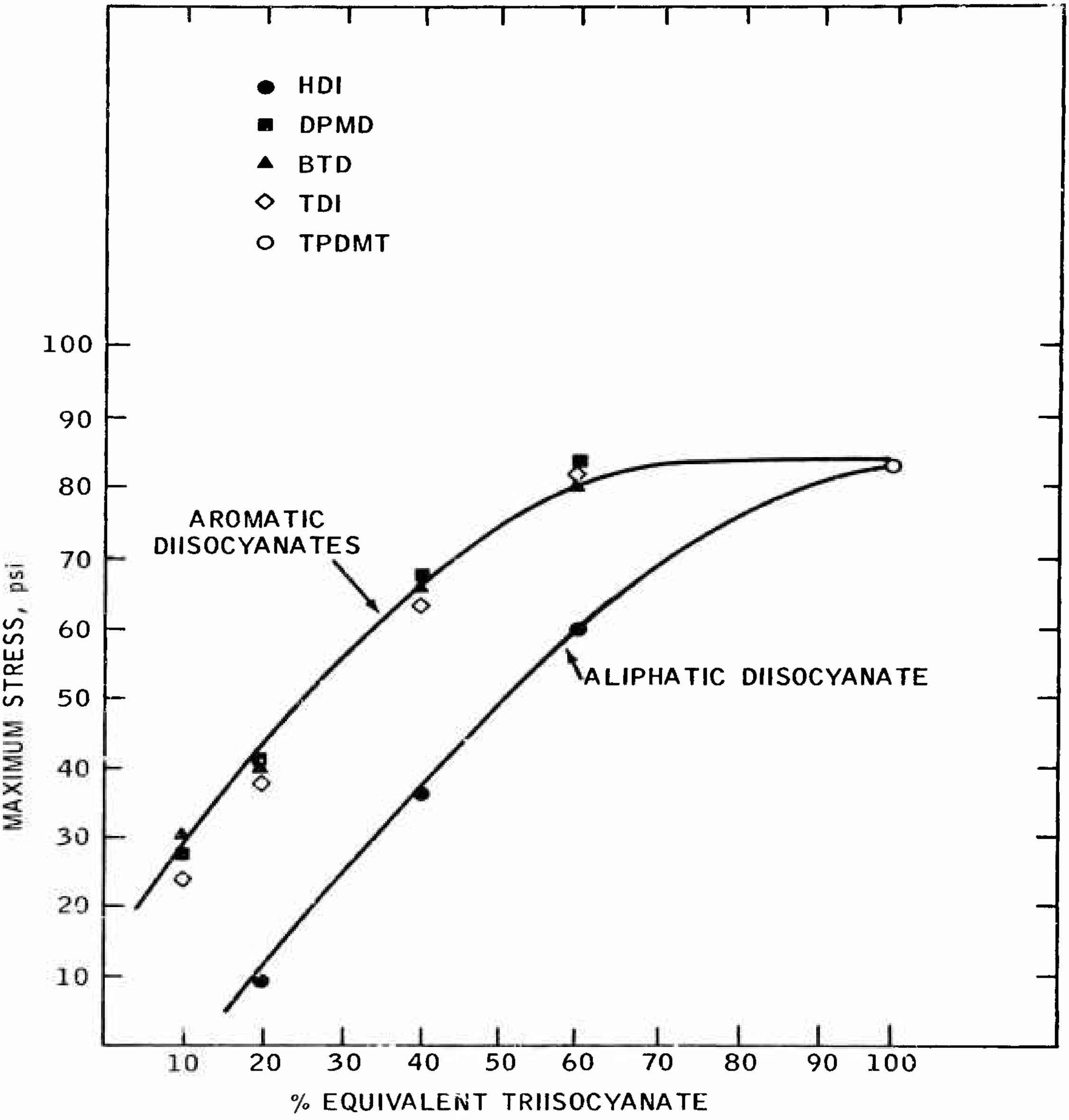


FIGURE 49

DEPENDENCE OF INITIAL MODULUS ON TRIISOCYANATE LEVEL AT AMBIENT TEMPERATURE

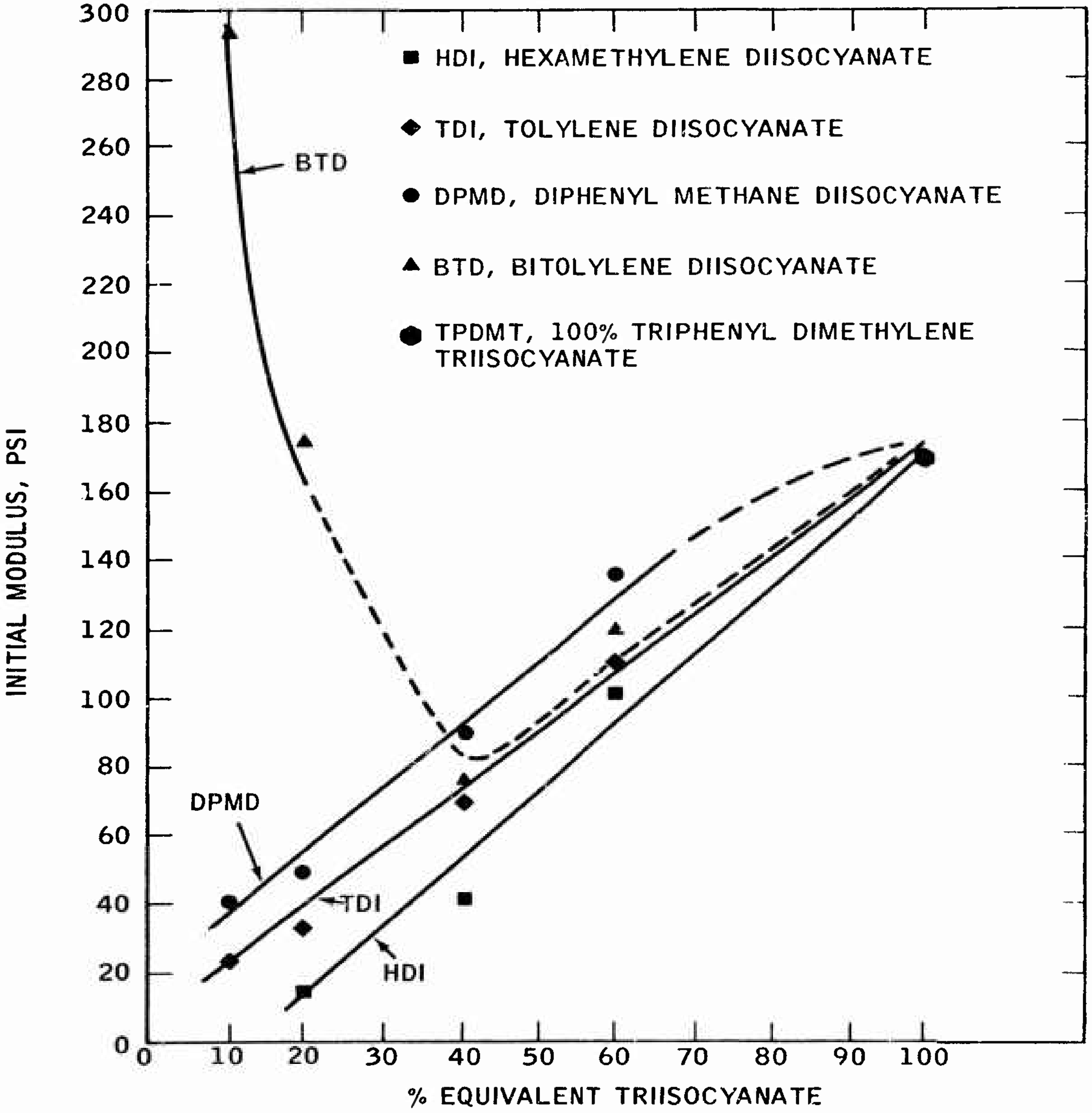
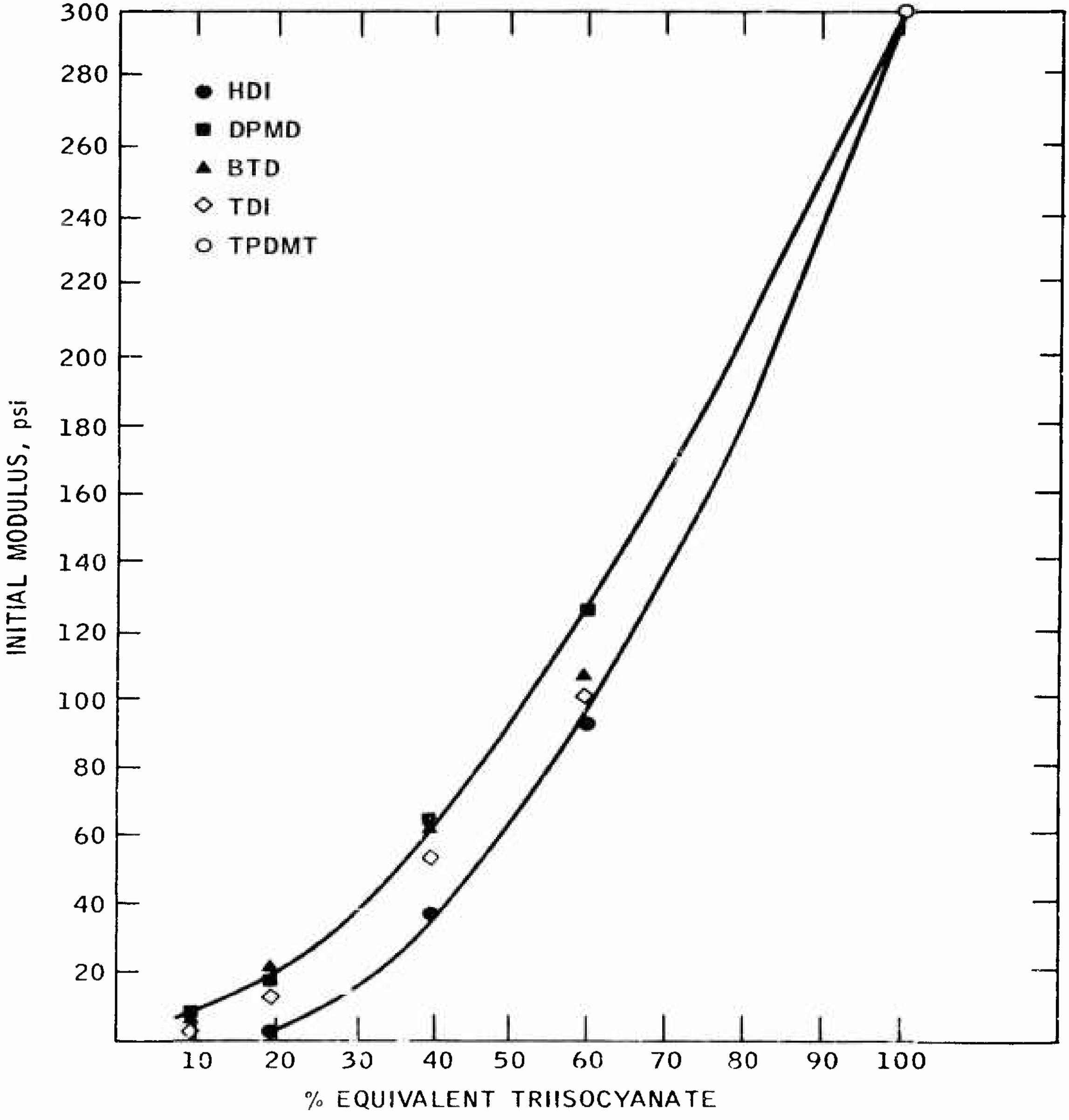


FIGURE 50

DEPENDENCE OF INITIAL MODULUS ON TRIISOCYANATE LEVEL AT 180°F USING FOUR DIFFERENT DIISOCYANATE CHAIN EXTENDERS



Shore "A" Hardness (Figure 51)

- The Shore "A" hardness also shows an essentially linear increase with increase in triisocyanate level for HDI, TDI and DPMD. BTD again shows a maximum at the high diisocyanate level reaching a minimum at 20 to 40 equivalent % triisocyanate. Both the initial modulus and the Shore "A" hardness show the same directional dependence on triisocyanate level for the four diisocyanates.

In summary then, it can be stated that aromatic diisocyanates give better mechanical properties at 180°F as well as at ambient temperature than aliphatic diisocyanates. The use of aromatic diisocyanates result in higher maximum stress levels at lower triisocyanate levels (lower crosslink density) and hence permits higher maximum strain levels.

FIGURE 51

DEPENDENCE OF SHORE "A" HARDNESS ON TRIISOCYANATE LEVEL AT AMBIENT TEMPERATURE

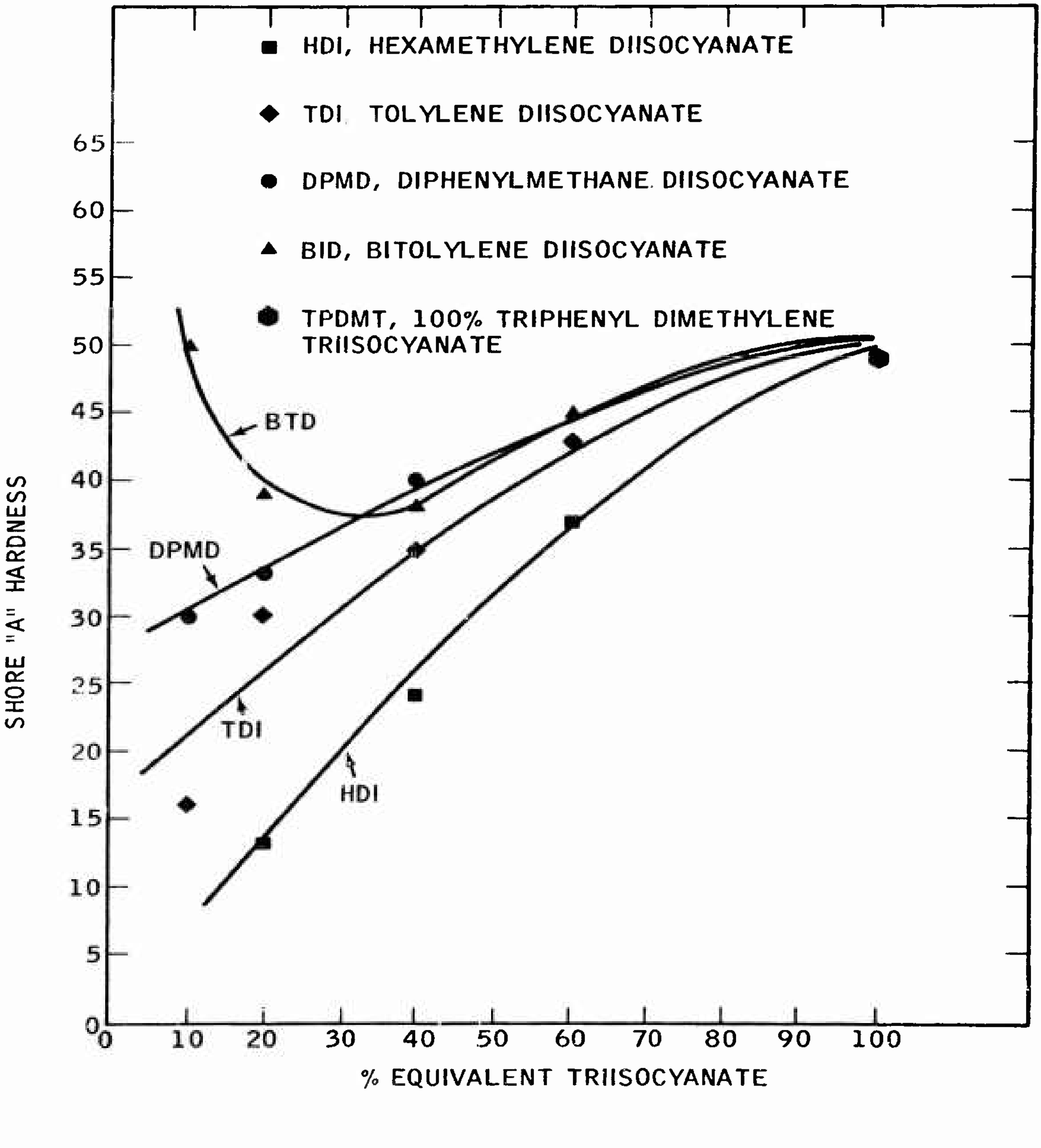


TABLE IL

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE FOR OH-TELAGEN-S, LOT 742811A, CURED WITH HEXAMETHYLENE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE

Di-/Triisocyanate Equivalent Ratio	Shore "A"	*Max. Stress (Psi)	**% Strain at Max. Stress	Initial Modulus (Psi)
9/1	---------------- Too soft and tacky to be tested ----------------			
8/2	13	41	980	14.0
6/4	24	144	480	41.5
4/6	37	156	240	101.0
100% Triisocyanate	49	190	140	169

---

* Equals stress at break

** Equals strain at break

TABLE L

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE FOR OH-TELAGEN-S, LOT 7428011A, CURED WITH DIPHENYLMETHANE DIISOCYANATE/TRIPHENYL DIMETHYL TRIISOCYANATE

Di-/Triisocyanate Equivalent Ratio	Shore "A"	*Max. Stress (Psi)	**% Strain at Max. Stress	Initial Modulus (Psi)
9/1	30	214	1240	40
8/2	33	199	760	49
6/4	40	215	400	89
4/6	43	214	260	135
100% Triisocyanate	49	190	140	169

---

* Equals stress at break

** Equals strain at break

TABLE LI

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE FOR FOR OH-TELAGEN-S, LOT 7428011A, CURED WITH TOLYLENE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE

Di-/Triisocyanate Equivalent Ratio	Shore "A"	*Max. Stress (Psi)	**% Strain at Max. Stress	Initial Modulus (Psi)
9/1	16	108	1430	22.8
8/2	30	163	795	33.6
6/4	35	187	400	69.6
4/6	43	161	226	109.5
100% Triisocyanate	49	190	140	169

---

* Equals stress at break

** Equals strain at break

TABLE LII

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE FOR OH-TELAGEN-S, LOT 742811A, CURED WITH BITOLYLENE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE

Di-/Triisocyanate Equivalent Ratio	Shore "A"	*Max. Stress (Psi)	**% Strain at Max. Stress	Initial Modulus (Psi)
9/1	50	334	1550	292
8/2	39	290	740	174
6/4	38	140	330	76
4/6	45	177	240	118
100% Triisocyanate	49	190	140	169

---

* Equals stress at break

** Equals strain at break

TABLE LIII

MECHANICAL PROPERTIES AT 180°F FOR OH-TELAGEN-S, LOT 742811A, CURED WITH HEXAMETHYLENE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE

Di-Triisocyanate Equivalent Ratio	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	------------ To soft to measure ----------------		
8/2	9	600	2.3
6/4	36	183	37.0
4/6	60	97	93.0
100% Triisocyanate	83	37	300

TABLE LIV

MECHANICAL PROPERTIES AT 180°F FOR OH-TELAGEN-S, LOT 742811A, CURED WITH DIPHENYL METHANE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE

Di-/Triisocyanate Equivalent Ratio	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	27	1070	6.7
8/2	41	455	17.2
6/4	67	185	63.0
4/6	84	107	124
100% Triisocyanate	83	37	300

TABLE LV

MECHANICAL PROPERTIES AT 180°F FOR OH-TELAGEN-S, LOT 742811A, CURED WITH TOLYLENE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE

Di-/Triisocyanate Equivalent Ratio	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	24	1300	2.4
8/2	37	510	12.6
6/4	63	180	52.4
4/6	82	140	100
100% Triisocyanate	83	37	300

TABLE LVI

MECHANICAL PROPERTIES AT 180°F FOR OH-TELAGEN-S LOT 742811A, CURED WITH BITOLYLENE DIISOCYANATE/TRIPHENYL DIMETHYLENE TRIISOCYANATE

Di-/Triisocyanate Equivalent Ratio	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	30	1260	6.5
8/2	40	420	21.1
6/4	65	167	62.5
4/6	81	106	106
100% Triisocyanate	83	37	300

3.2. Mechanical Properties of Gumstocks Aged at 275°F in a Nitrogen Atmosphere for 7 Days

To determine whether any of the above four diisocyanate structures would show optimum heat aging properties, the cured OH-Telagen-S gumstocks described above were heat aged at 275°F in a nitrogen atmosphere for 7 days. The samples were kept in a temperature controlled oven and a small flow of nitrogen was maintained during the heat aging period. Mechanical properties were subsequently obtained at ambient temperature. The data are summarized in Tables LVII through LX. To facilitate a comparison of the mechanical properties of aged vs. unaged samples, we have graphically represented maximum stress, maximum strain, initial modulus and Shore "A" hardness both before and after heat aging for each of the four cure systems. As shown in Figures 52 through 55 the above mechanical parameters reveal only minor changes upon thermal aging at 275°F.

The maximum strain retained its singular dependence on triisocyanate level.

The maximum stress showed again the dual dependence on both triisocyanate level and structure of the diisocyanate. For a given di-/triisocyanate system there was essentially the same dependence of maximum stress on triisocyanate concentration both before and after heat aging.

Both the initial modulus and hardness showed the same dependence on triisocyanate level and diisocyanate structure before and after heat aging.

These data show that urethane binders will have adequate thermal stability at the 275°F temperature level over the stated test period (7 days). Based on these data also there is no preferred diisocyanate structure from the standpoint of heat aging properties at 275°F. All cure systems have shown excellent thermal aging behavior in the OH-Telagen-S gumstock.

TABLE LVII

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE AFTER HEAT AGING AT 275°F FOR 7 DAYS IN N_2

Gumstock: OH-Telagen-S, Lot 742811A, Cured with Hexamethylene Diisocyanate/Triphenyl Dimethylene Triisocyanate

Di-/Triisocyanate Equivalent Ratio	Shore "A"	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	----------- Too soft and tacky to be tested -----------			
8/2	12	67	990	18
6/4	27	145	500	41
4/6	35	148	265	93
100% Triisocyanate	47	185	190	154

TABLE LVIII

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE AFTER HEAT AGING AT 275°F FOR 7 DAYS IN N_2

Gumstock: OH-Telagen-S, Lot 742811A, Cured with Diphenyl Methane Diisocyanate/Triphenyl Dimethylene Triisocyanate

Di-/Triisocyanate Equivalent Ratio	Shore "A"	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	33	227	1230	40
8/2	37	200	760	50
6/4	40	215	410	89
4/6	43	214	290	110
100% Triisocyanate	47	185	190	154

TABLE LIX

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE AFTER HEAT AGING AT 275°F FOR 7 DAYS IN N_2

Gumstock: OH-Telagen-S, Lot 742811A Cured with Tolylene Diisocyanate/Triphenyl Dimethylene Triisocyanate

Di-/Triisocyanate Equivalent Ratio	Shore "A"	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	20	95	2040	19
8/2	27	200	980	25
6/4	30	173	470	55
4/6	35	188	300	101
100% Triisocyanate	47	185	190	154

TABLE LX

MECHANICAL PROPERTIES AT AMBIENT TEMPERATURE AFTER HEAT AGING AT 275°F FOR 7 DAYS IN N_2

Gumstock: OH-Telagen-S, Lot 742811A Cured With Bitolylene Diisocyanate/Triphenyl Dimethylene Triisocyanate

Di-/Triisocyanate Equivalent Ratio	Shore "A"	Max. Stress (Psi)	% Strain at Max. Stress	Initial Modulus (Psi)
9/1	50	290	1490	267
8/2	40	380	830	130
6/4	35	130	380	69
4/6	38	190	290	105
100% Triisocyanate	47	185	190	154

Effect of heat aging at 275°F (7 days) on mechanical properties of OH-Telagen-S gumstock, lot 742 811A.

Chain extender: <u>hexamethylene diisocyanate</u>

Crosslinker: triphenyl dimethylene triisocyanate

Figure 52a Dependence of % strain at maximum stress on triisocyanate level.

Figure 52b Dependence of maximum stress on triisocyanate level.

Figure 52c Dependence of initial modulus on triisocyanate level.

Figure 52d Dependence of Shore "A" hardness on triisocyanate level.

FIGURE 52a

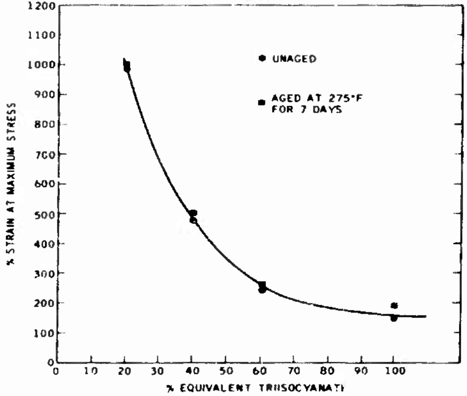


FIGURE 52b

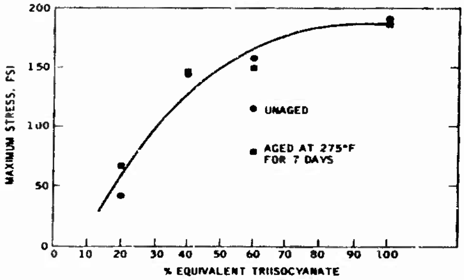


FIGURE 52c

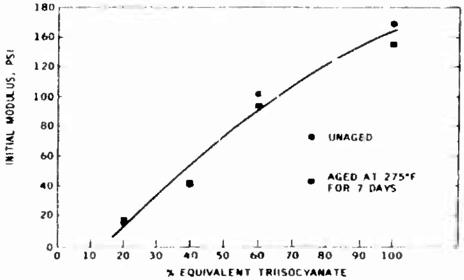
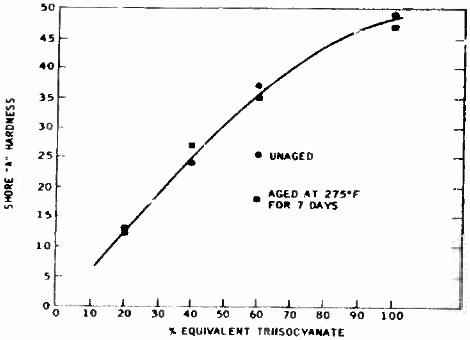


FIGURE 52d



Effect of heat aging at 275°F (7 days) on mechanical properties of OH-Telagen-S gumstock, lot 742 811A.

Chain extender: tolylene diisocyanate

Crosslinker: triphenyl dimethylene triisocyanate

Figure 53a Dependence of % strain at maximum stress on triisocyanate level.

Figure 53b Dependence of maximum stress on triisocyanate level.

Figure 53c Dependence of initial modulus on triisocyanate level.

Figure 53d Dependence of Shore "A" hardness on triisocyanate level.

FIGURE 53a

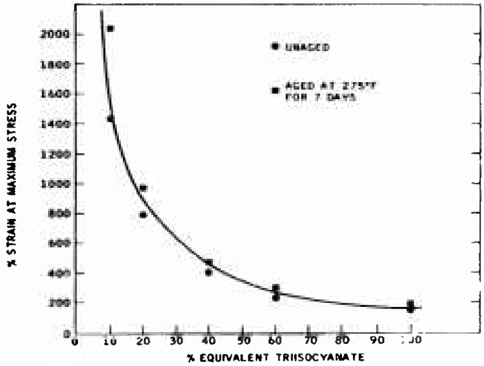


FIGURE 53b

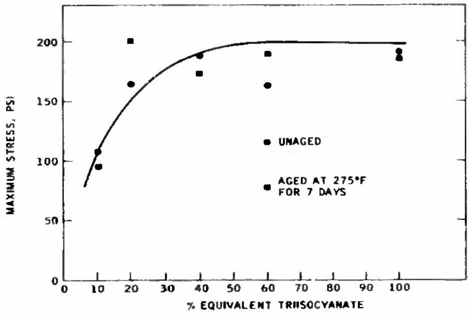


FIGURE 53c

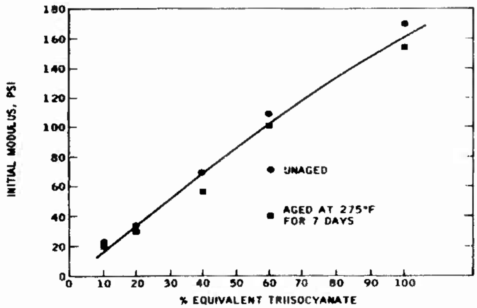
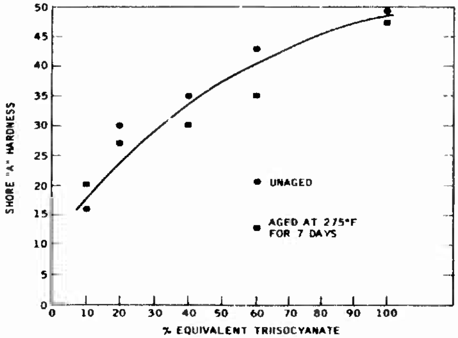


FIGURE 53d



Effect of heat aging at 275°F (7 days) on mechanical properties of OH-Telagen-S gumstock, lot 742 811A.

Chain extender: <u>diphenyl methane diisocyanate</u>
Crosslinker: triphenyl dimethylene triisocyanate

Figure 54a Dependence of % strain at maximum stress on triisocyanate level.

Figure 54b Dependence of maximum stress on triisocyanate level.

Figure 54c Dependence of initial modulus on triisocyanate level.

Figure 54d Dependence of Shore "A" hardness on triisocyanate level.

FIGURE 54a

EFFECT OF HEAT AGING AT 275°F (7 DAYS) IN N_2 ON STRAIN AT MAXIMUM STRESS AT AMBIENT TEMPERATURE

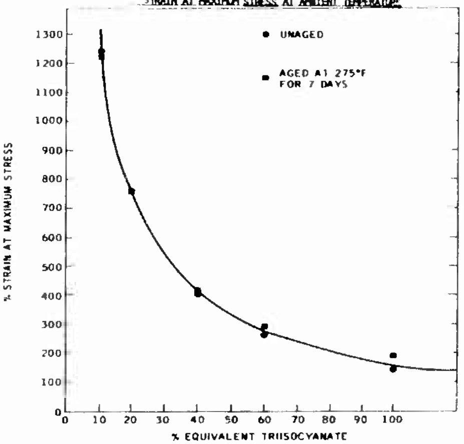


FIGURE 54b

EFFECT OF HEAT AGING AT 275°F (7 DAYS) IN N_2 ON MAXIMUM STRESS AT AMBIENT TEMPERATURE

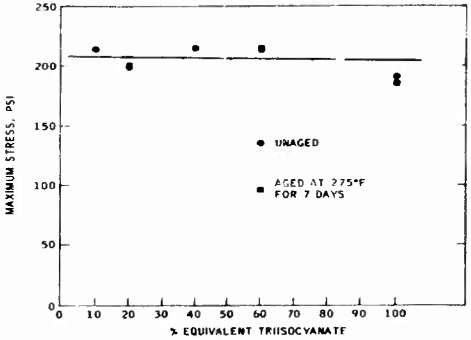


FIGURE 54c

EFFECT OF HEAT AGING AT 275°F (7 DAYS) IN N_2 ON INITIAL MODULUS AT AMBIENT TEMPERATURE

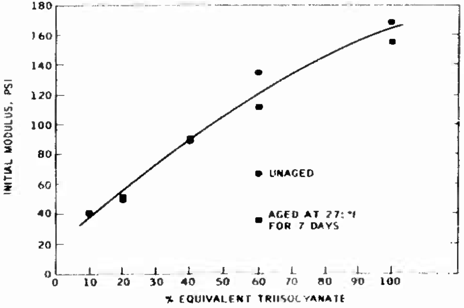
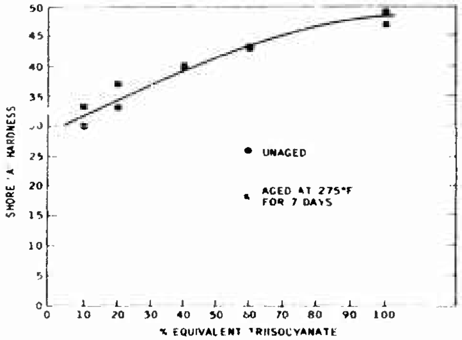


FIGURE 54d

EFFECT OF HEAT AGING AT 275°F (7 DAYS) IN N_2 ON SHORE "A" HARDNESS AT AMBIENT TEMPERATURE



Effect of heat aging at 275°F (7 days) on mechanical properties of OH-Telagen-S gumstock, lot 742 811A.

Chain extender: bitolylene diisocyanate

Crosslinker: triphenyl dimethylene triisocyanate

Figure 55a Dependence of % strain at maximum stress on triisocyanate level.

Figure 55b Dependence of maximum stress on triisocyanate level.

Figure 55c Dependence of initial modulus on triisocyanate level.

Figure 55d Dependence of Shore "A" hardness on triisocyanate level.

FIGURE 55a

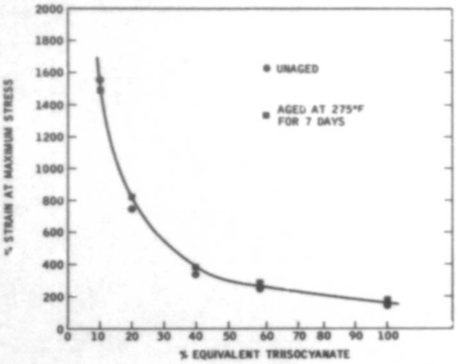


FIGURE 55b

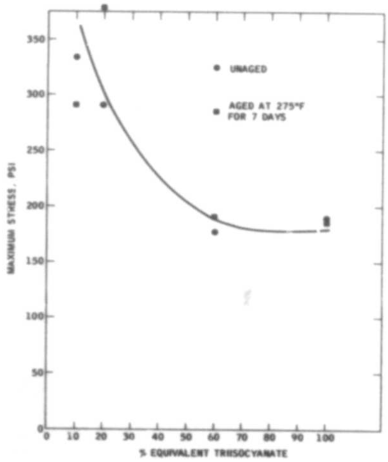


FIGURE 55c

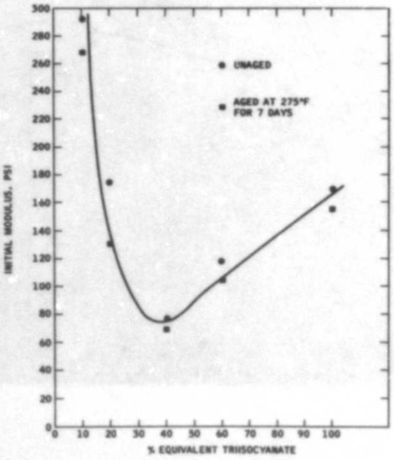
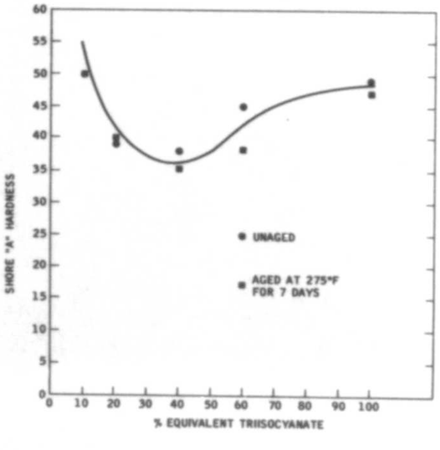


FIGURE 55d



V. APPENDIX

A. EXPERIMENTAL DETAILS

1. Preparation of N-Sulfonyl Aziridines

a. Preparation of N-[Aryl Sulfonyl]-Aziridines

Aryl sulfonyl chloride (0.02 mole) and ethyl ether (50 ml) was added in 1 hr. to a stirred solution (0°C) of an aziridine (0.02 mole) and triethylamine (0.02 mole) in ethyl ether (50 ml). The solutions were stored at -20°C overnight. The ether solution was washed with water until neutral, dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness in a Roto-Vac.

The crude products were recrystallized from carbon tetrachloride-pentane.

b. Preparation of N-Butanesulfonyl-2-Methyl Aziridine

N-Butanesulfonyl-2-methylaziridine was prepared by reacting 2-methylaziridine and 1-butane sulfonyl chloride in the manner described above.

The crude liquid was distilled at 65-67°C at 0.1 mm Hg.

c. Preparation of N-Butanesulfonyl-2,2-Dimethyl Aziridine

N-Butanesulfonyl-2,2-dimethyl aziridine was prepared by reacting 2,2-dimethyl aziridine and 1-butanesulfonyl chloride in the same manner described above.

The liquid was distilled at 86-86°C at 0.17 mm Hg.

d. Preparation of 1,3-Benzene Bis-Sulfonyl cis-2,3-Dimethyl Aziridine

The 1,3-benzene disulfonyl chloride was recrystallized from benzene-pentane, m.p. 63.0-63.5°C. The same procedure was used as described above to make the difunctional derivative except that equivalent amounts of dichloride to aziridine to triethyl amine was used. The crude product was recrystallized from 80% benzene-20% methylene chloride solvent pair by the slow addition of cold pentane; m.p. 140-141, 60% yield.

e. Preparation of 1,3,5-Benzene Tris-Sulfonyl cis-and trans-2,3-Dimethyl Aziridine

The 1,3,5-benzene trisulfonyl chloride was recrystallized from hot benzene. Equivalent stoichiometry was used and the procedure followed was the same as that described above except that tetrahydrofuran was used as solvent. Recrystallization from benzene gave a 37% yield of product, m.p. 188-189°C.

The trans isomer was similarly prepared. An 8% yield from benzene-pentane was recovered, m.p. 122.5-123°C.

2. Preparation of N-Acyl Aziridines

a. Preparation of N-[p-Nitrobenzoyl]-Aziridines and N-[p-Toluyl]-Aziridines

The same conditions used to prepare the N-aryl sulfonyl aziridines mentioned above were used here. p-Nitro benzoyl chloride was purified by recrystallization from benzene and p-toluyl chloride was purified by vacuum distillation. Yields and m.p. are shown in Table XXXIII (page 79).

b. Preparation of the Bis-cis-2,3-Dimethyl Aziridide of Adipic Acid

Freshly distilled adipoyl chloride (7.3 g) was dissolved in 50 ml of benzene and cooled to 0°C. A solution of 5.9 g of cis-2,3-dimethyl aziridine and 8.4 g of triethyl amine was slowly added. The filtered solution was stripped in vacuo and the crude solid taken up in carbon tetrachloride, washed with water, dried with magnesium sulfate and filtered. Pentane was added until the solution turned cloudy. Chilling to 0°C yielded crystals, m.p. 56-57°C, in 24% yield.

c. Preparation of 1,3,5-Benzene-Tris-Carbonyl-cis-2,3-Dimethyl Aziridine

Trimesoyl chloride (freshly vacuumed distilled) (15.6 g, 0.05 M) was dissolved in 60 ml of benzene and chilled. cis-2,3-Dimethyl aziridine (10.7 g, 0.15 M) and triethyl amine (15.15 g, 0.15 M) in 60 ml of benzene was added slowly. The reaction was stirred for 3 hrs at 0°C and 27 hrs at room temperature. The amine hydrochloride was removed by filtration and pentane added to the supernatant. Chilling yielded crystals which were further purified by recrystallization from carbon tetrachloride-pentane, m.p. 161-162.5°C. Yield was 53%.

3. Preparation of N-Carbamyl Aziridines

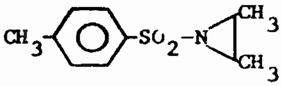
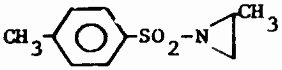
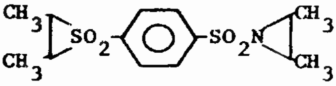
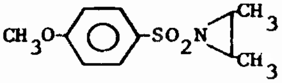
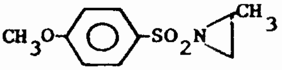
The N-carbamyl aziridines were made by adding 20% benzene solutions of the purified mono, di, or triisocyanate to a 20% benzene solution of the appropriate aziridine. Equivalent quantities were used and reaction was carried out at ice batch temperatures for 3-4 hrs. Removal of solvent in vacuo gave nearly quantitative yields of pure materials.

B. DETERMINATION OF AZIRIDINES BY TITRATION

The titration of N-substituted aziridines was done by the hydrobromic-acetic acid method of Durbetaki (1) and the tetrabutylammonium iodide-perchloric acid method of Jay (2). In Table I the results are shown for titration of N-sulfonyl aziridine using both techniques. Values represent the experimental/theory ratio. Precision was not as good as desired and probably could be improved with practice in establishing the end point.

TABLE I

N-SULFONYL AZIRIDINES

	HBr-HAC	$Bu_4N^+I^\ominus$
	--	.844 .871
	--	.925 .918
	--	.972 .968
	1.05 1.13	--
	1.00 1.00	--

The $Bu_4N^\oplus I^\ominus$ method involves adding a standardized perchloric acid-acetic acid solution to aziridine in chloroform with excess tetrabutyl ammonium iodide and crystal violet indicator. The hydrogen iodide is liberated by perchloric and opens the aziridine ring. Equivalency is detected by a sharp change in the color of crystal violet indicator.

In Table II results are shown for titration values using the $Bu_4N^\oplus I^\ominus$ method on four classes of N-substituted 2-methyl and cis-2,3-dimethyl aziridines.

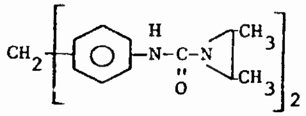
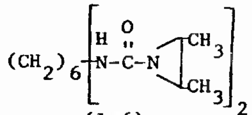
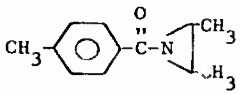
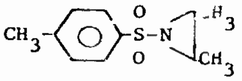
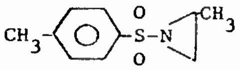
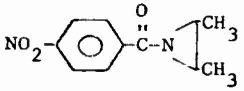
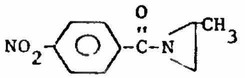
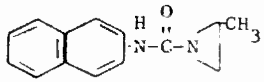
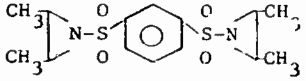
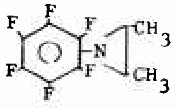
---

(1) A. J. Durbetaki, Anal. Chem. 28, 2000 (1956).

(2) R. R. Jay, Anal. Chem., 36, 667 (1964).

TABLE II

TITRATION DATA FOR AZIRIDINES USING NBu_4I (10% IN $CHCl_3$) AND $HClO_4$ (0.02456 N IN HOAc)

Compound	Meg. Aziridine N Theory	Meg. Aziridine N Exper.	Ratio exp/theor.
	0.2933 0.3600 0.6664 0.4974	0.3096 0.3321 0.6510 0.5157	1.055 0.9225 0.976 1.030
 (1,6)	0.6010 0.4950	0.6289 0.5435	1.045 1.078
	0.2638 0.2690	0.2563 0.2705	0.971 1.00
	0.2240 0.2225	0.1891 0.1939	0.844 0.871
	0.2323 0.2302	0.2152 0.2113	0.925 0.918
	0.2114 0.2230	0.2115 0.2231	1.00 1.00
	0.3038 0.2425	0.2885 0.2385	0.950 0.983
	0.2890 0.2310	0.2597 0.2330	0.899 1.009
	0.2890 0.2840	0.2810 0.2754	0.9720 0.9680
	0.2402 0.2348	0.2480 0.2430	1.077 1.081

APPENDIX C

INFRARED AND NMR SPECTRA

1. Representative Monofunctional Sulfonyl Aziridines

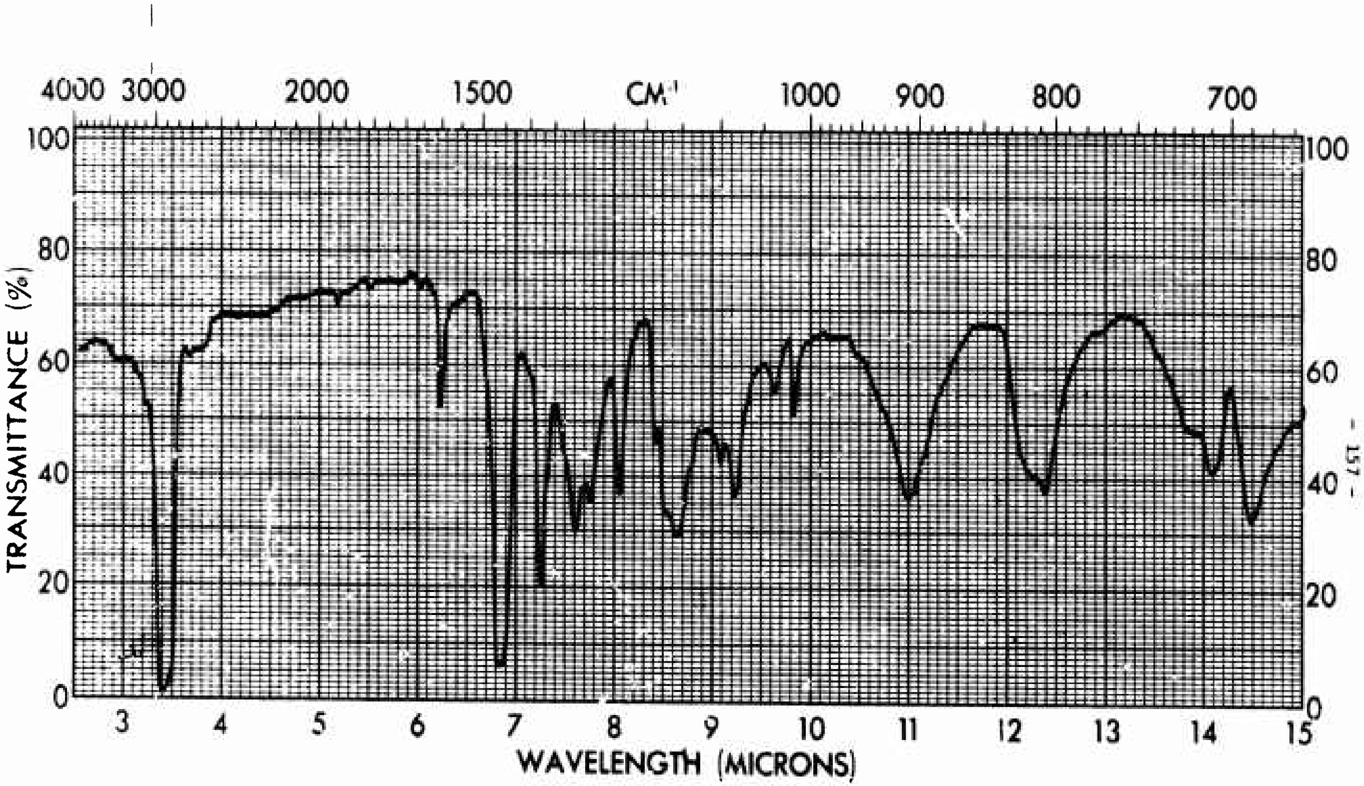


Figure 56. **Infrared spectrum of N-[p-toluene sulfonyl]-aziridine (nujol).**

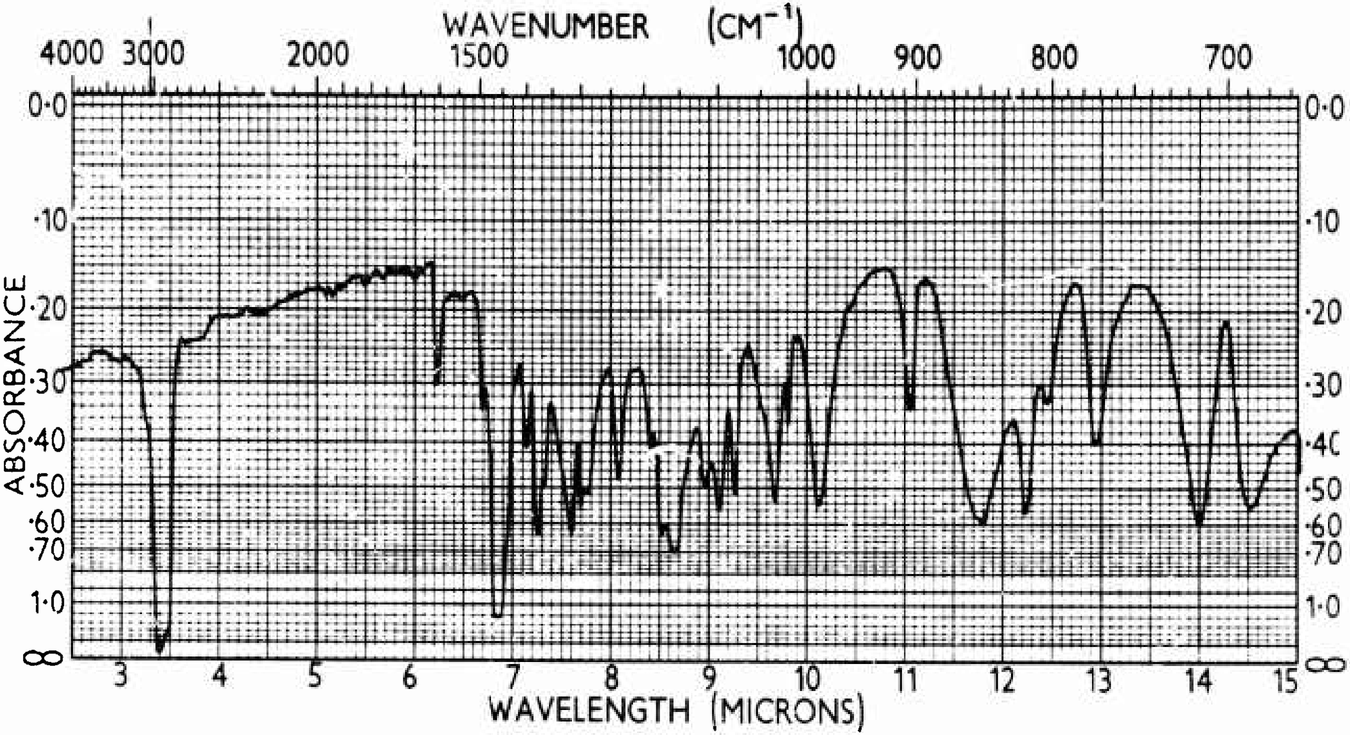


Figure 57. Infrared spectrum of N-[p-toluene sulfonyl]-2-methylaziridine (nujol).

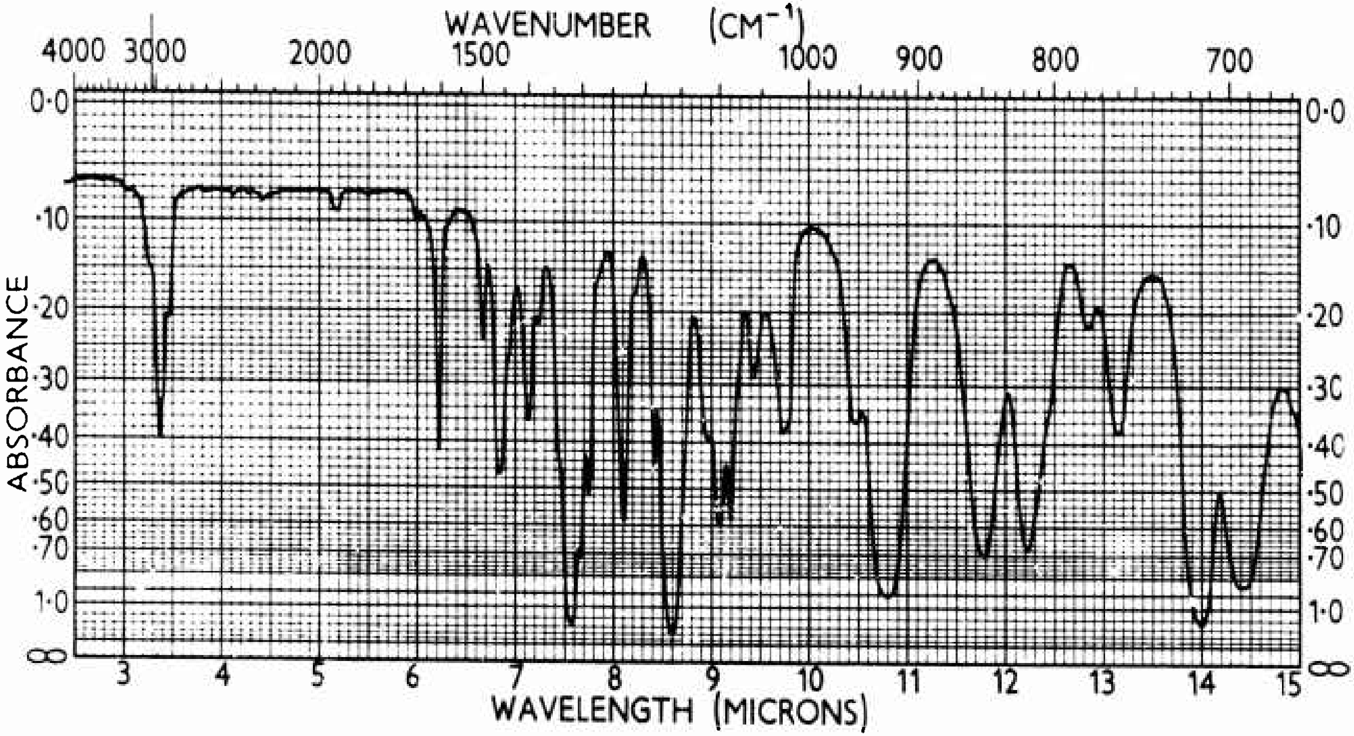


Figure 58. Infrared spectrum of N-[p-toluene sulfonyl]-2-ethylaziridine (neat).

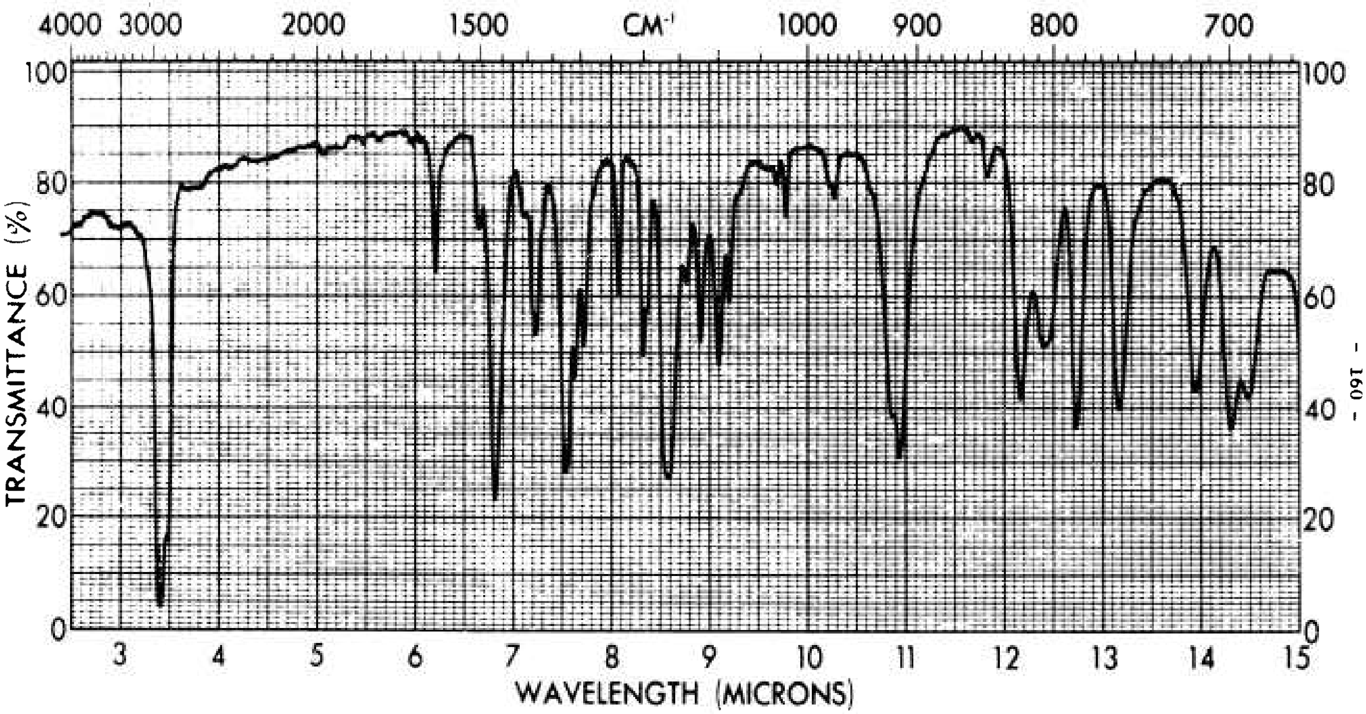


Figure 59. Infrared spectrum of N-[p-toluene sulfonyl]-2-phenyl aziridine (nujol).

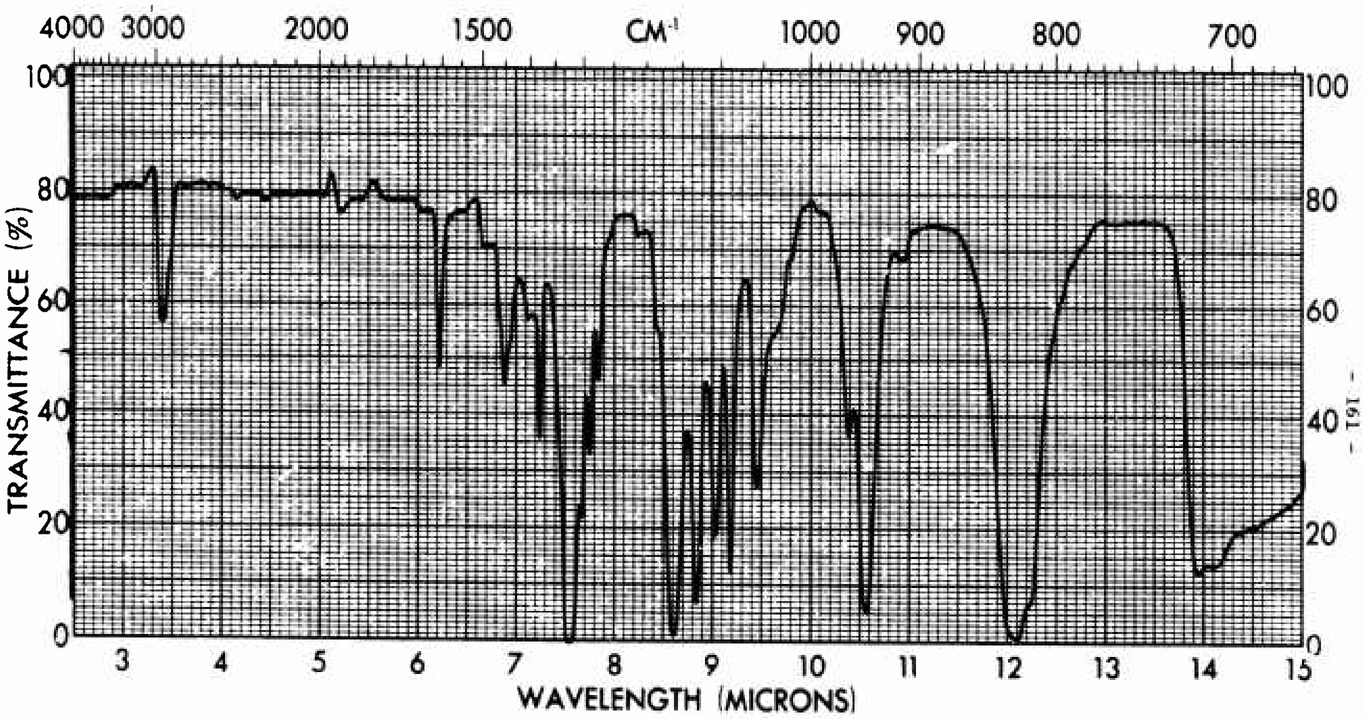


Figure 60. Infrared spectrum of N-[p-toluenesulfonyl]-2,2-dimethylaziridine (benzene vs. benzene).

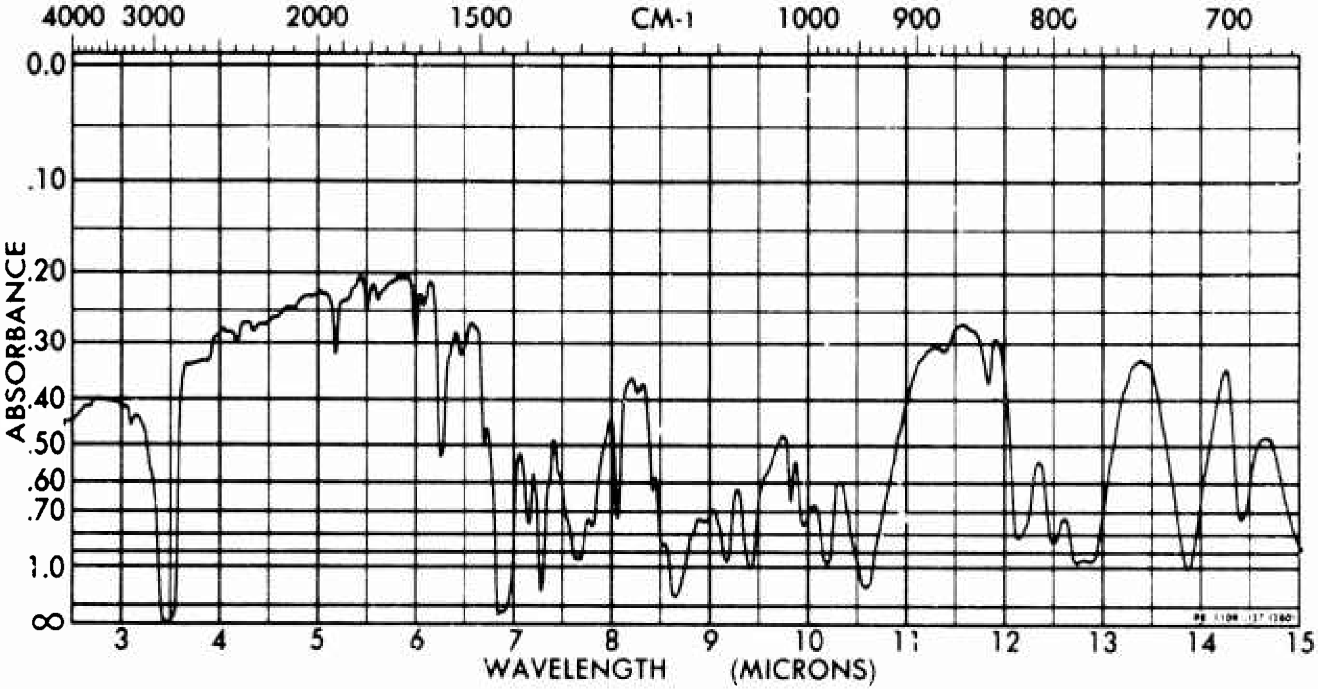


Figure 61. Infrared spectrum of N-[p-toluenesulfonyl]-cis-2,3-dimethylaziridine (nujol)

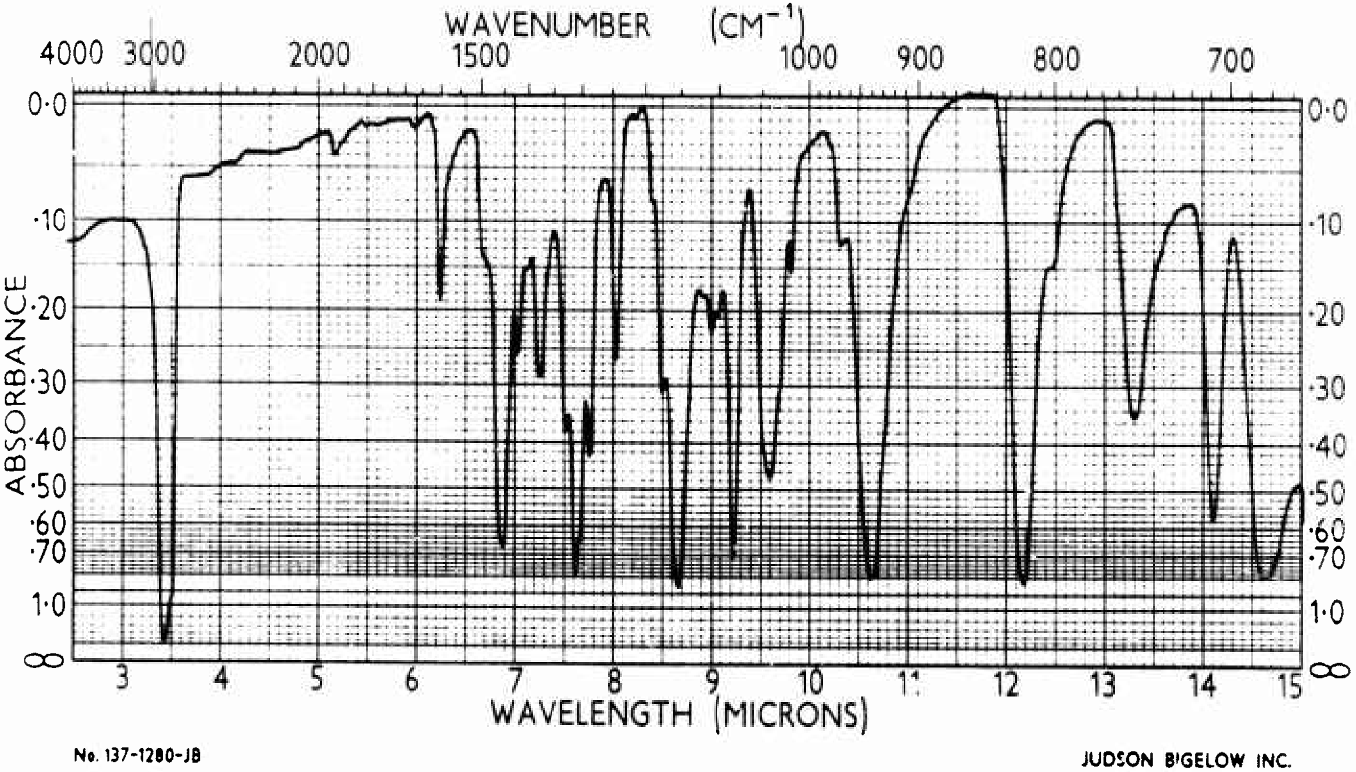


Figure 62. Infrared spectrum of N-[p-toluenesulfonyl]-trans-2,3-dimethylaziridine (nujol)

2. Di- and Trifunctional Sulfonyl Aziridines

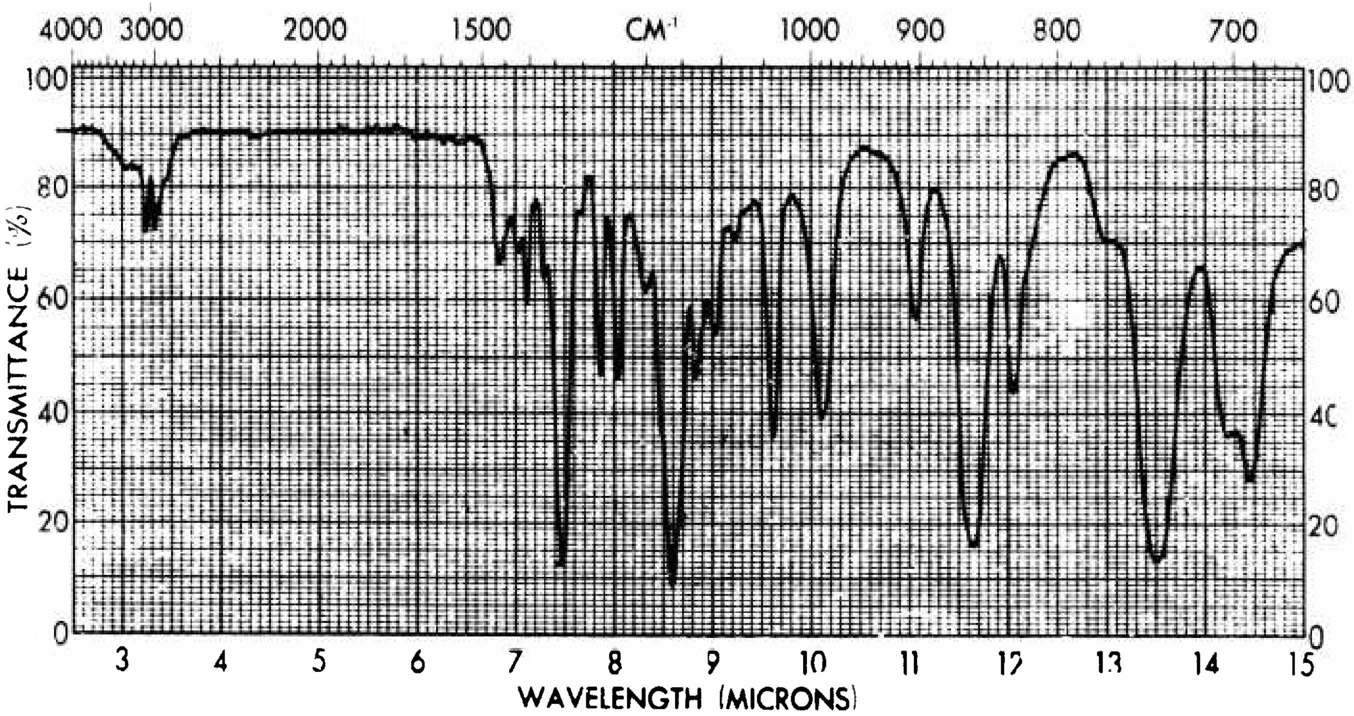


Figure 63. 1,3,5-tris-benzene-[N-sulfonyl-2-methylaziridine] (carbon dichloride)

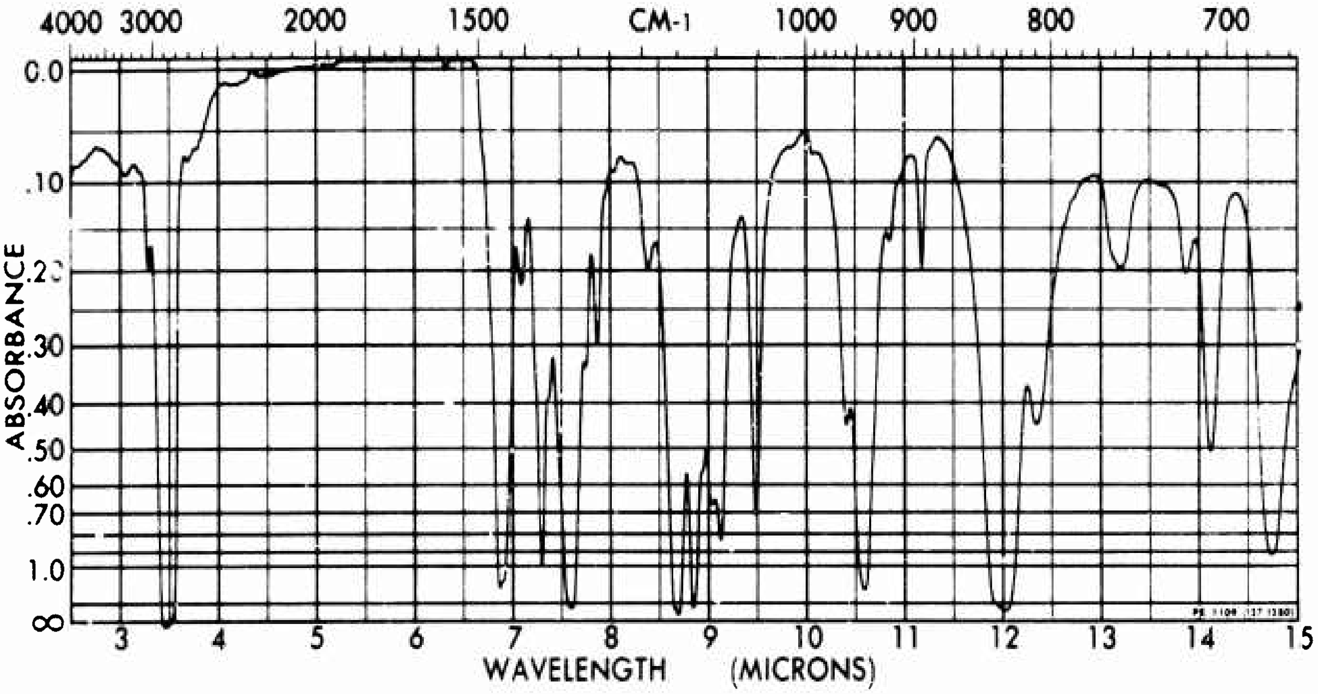


Figure 64. 1,3,5-tris-benzene-[N-sulfonyl-2,2-dimethylaziridine] (nujol)

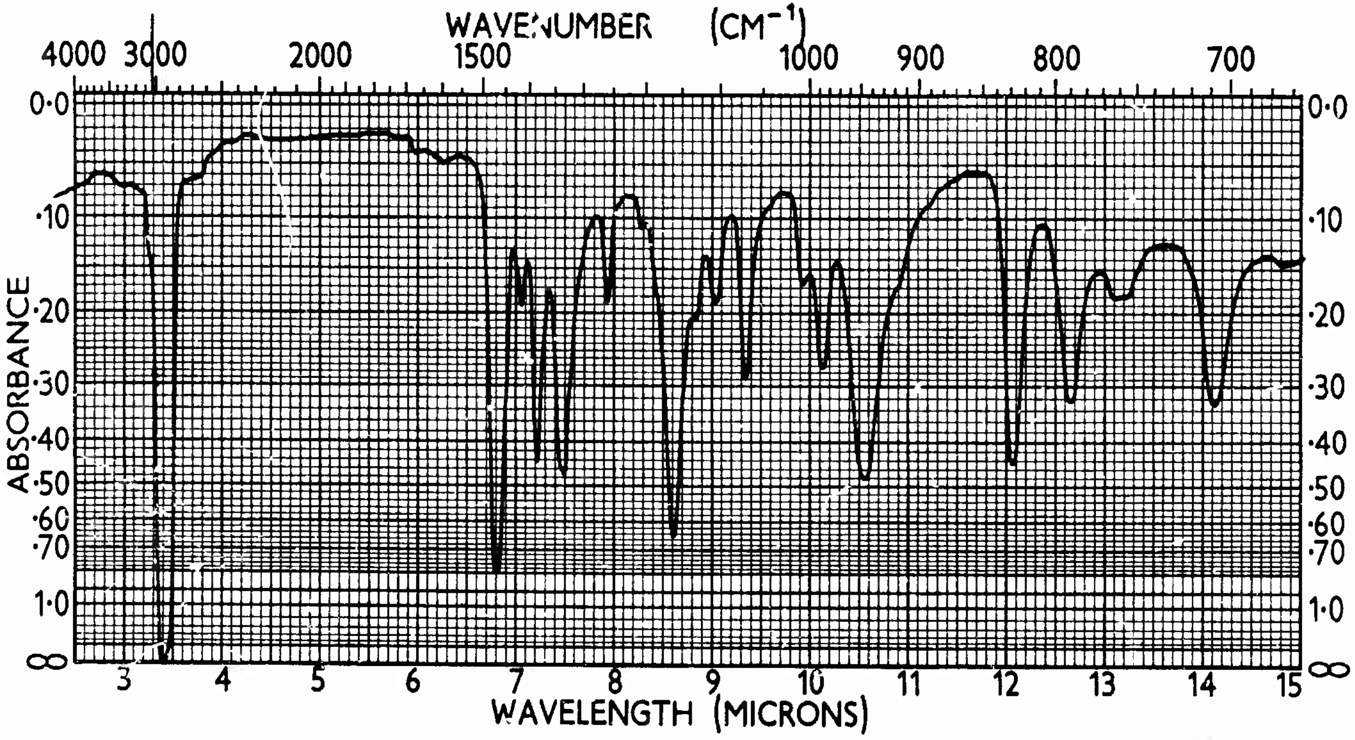


Figure 65. Infrared spectrum of 1,3,5-tris-benzene-[N-sulfonyl-cis-2,3-dimethyl aziridine] (nujol)

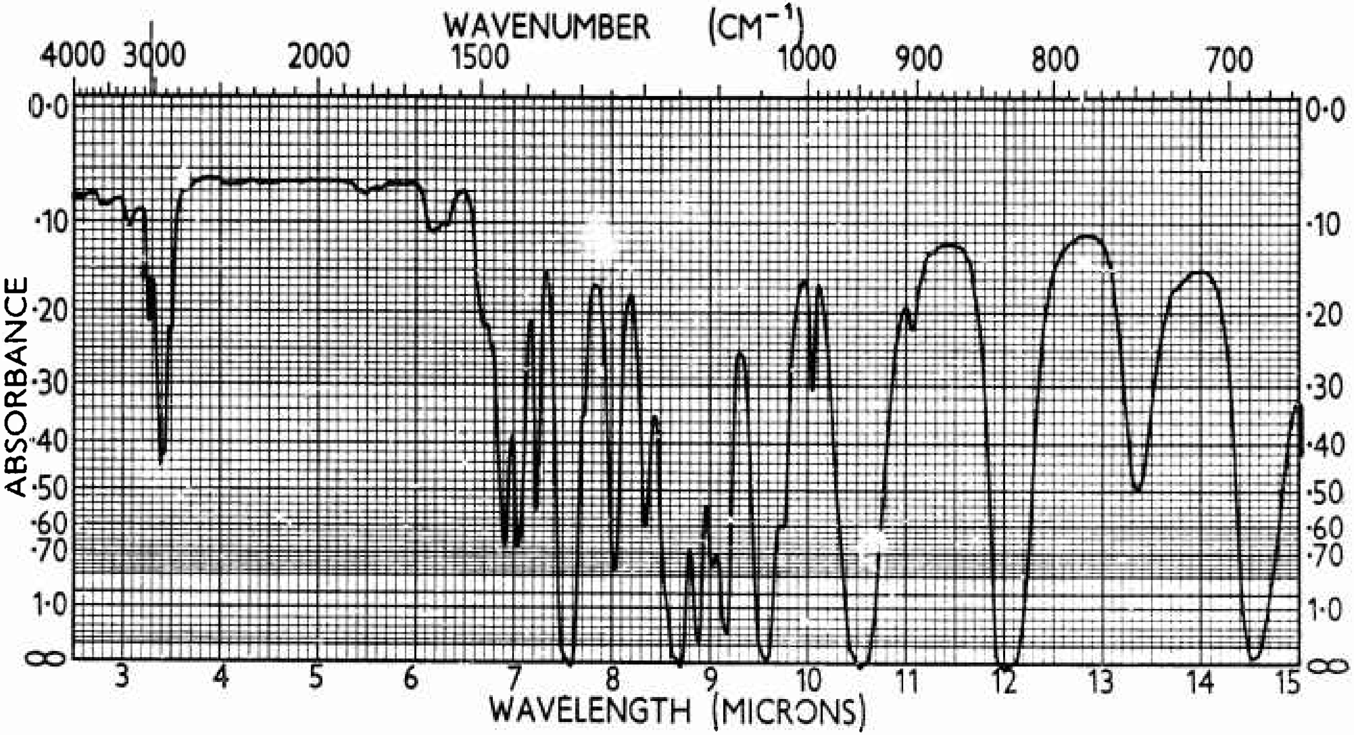


Figure 66. Infrared spectrum of 1,3,5-tris-benzene sulfonyl-trans-2,3-dimethylaziridine (oil)

3. Di- and Trifunctional N-Acyl Aziridines

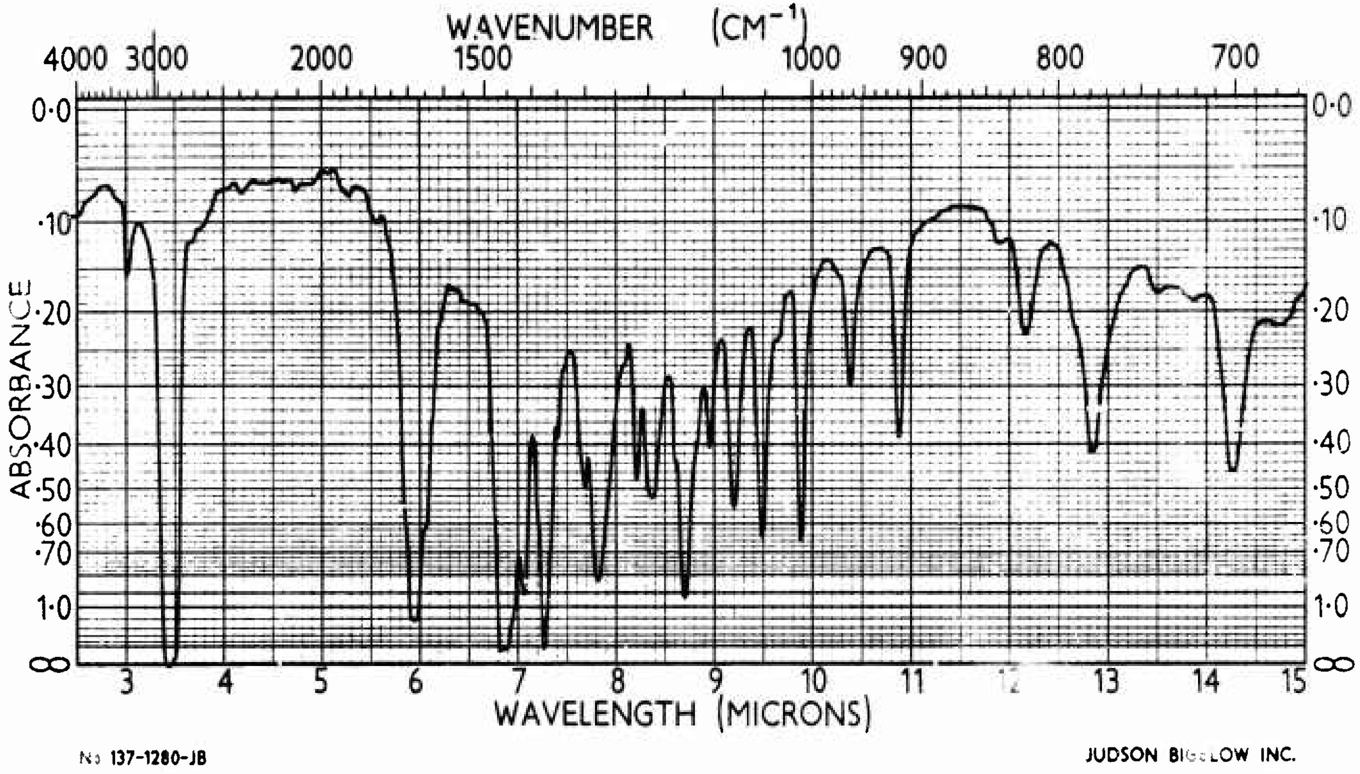


Figure 67. Infrared spectrum of N,N'-[cis-2,3-butylene]-adipamide (nujol)

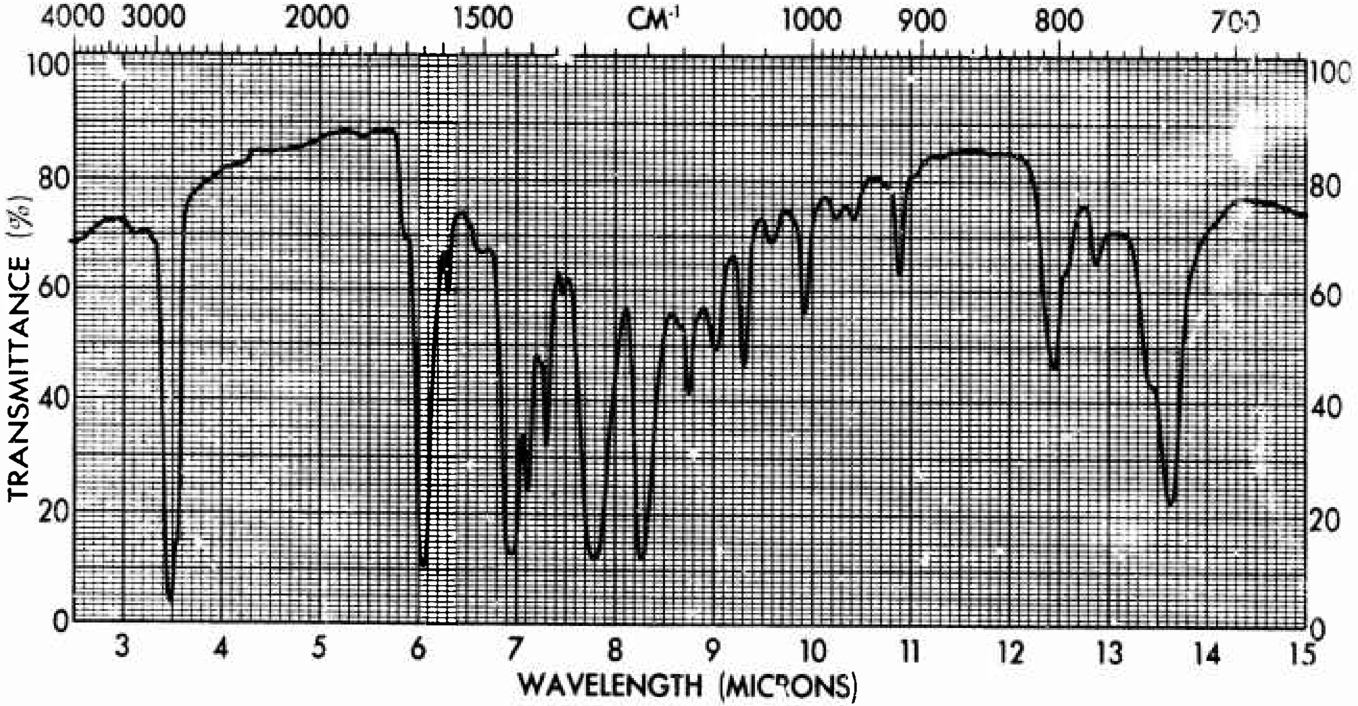


Figure 68. Infrared spectrum of 1,3,5-benzene tris-[carboxy(cis-2,3-dimethyl)aziridine] (nujol)

4. Di- and Trifunctional N-Carbamyl Aziridines

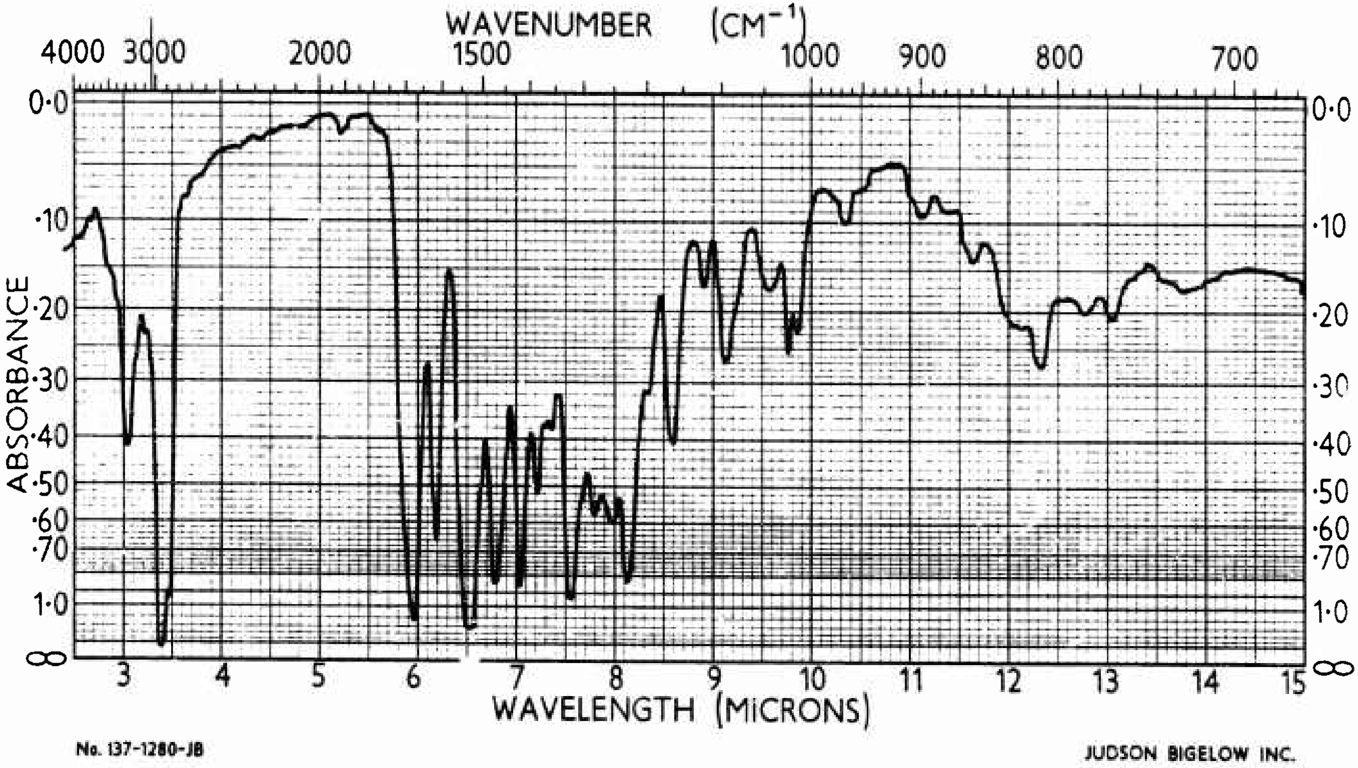


Figure 69. Infrared spectrum of tris-[p-[N,N-(cis,2,3-butylene)ureido]phenyl methane (nujol)

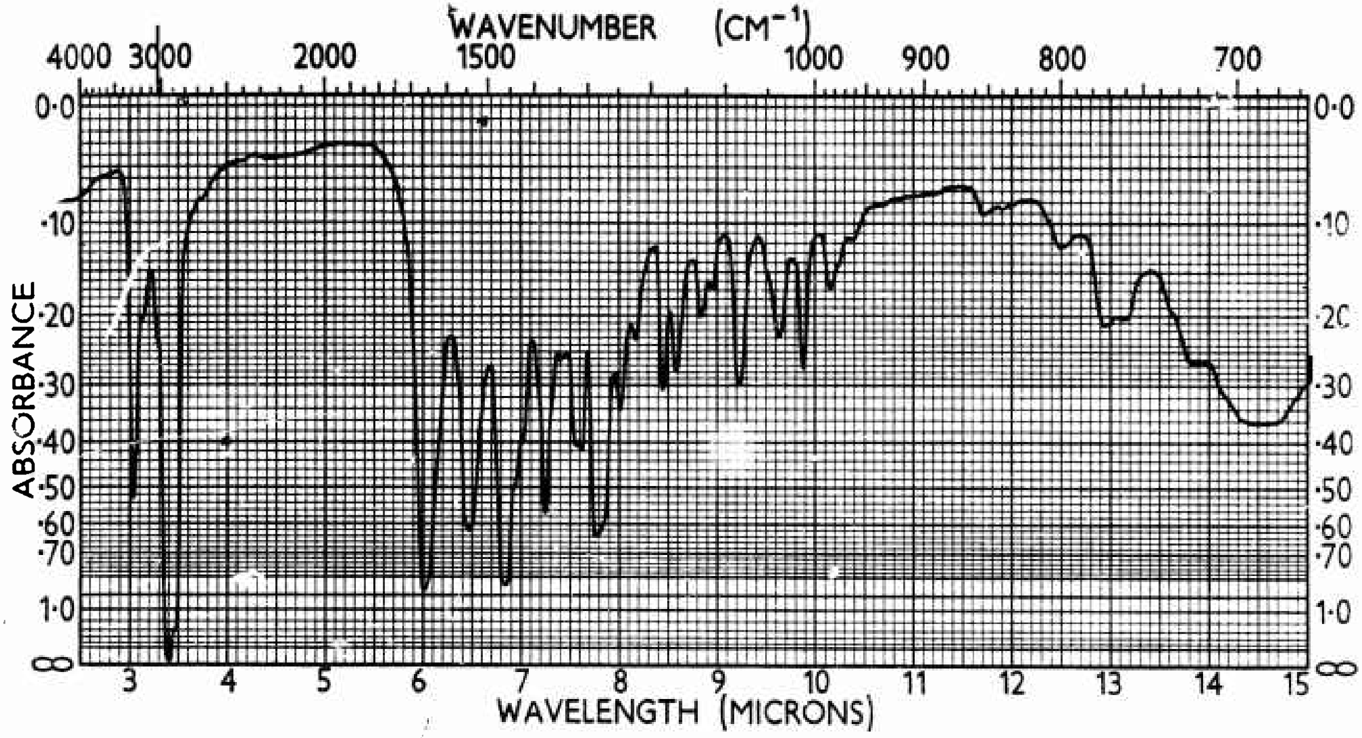


Figure 70. Infrared spectrum of N,N'-hexamethylene bis-carbamyl-cis-2,3-dimethylaziridine (nujol)

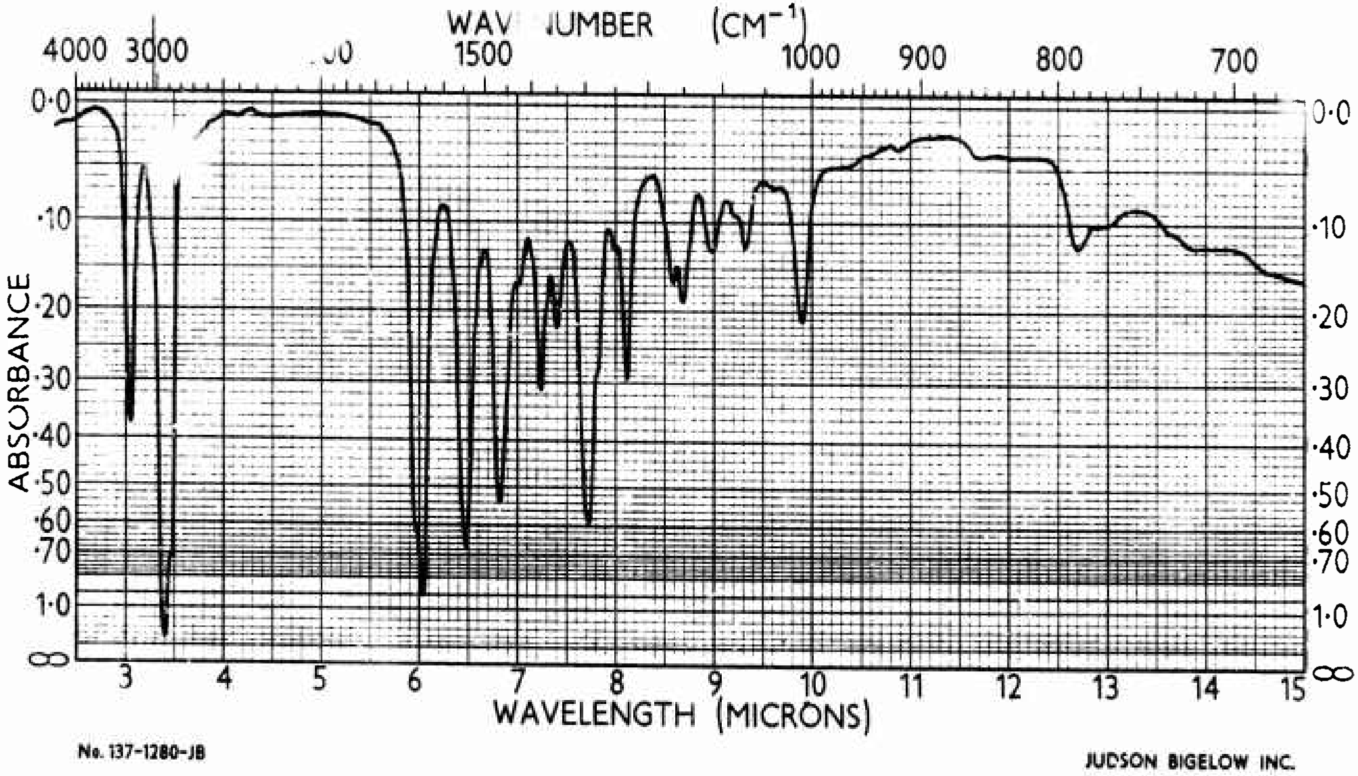


Figure 71. Infrared spectrum of 1,3,5-cyclohexane tris-carbamyl-cis-2,3-dimethylaziridine (nujol)

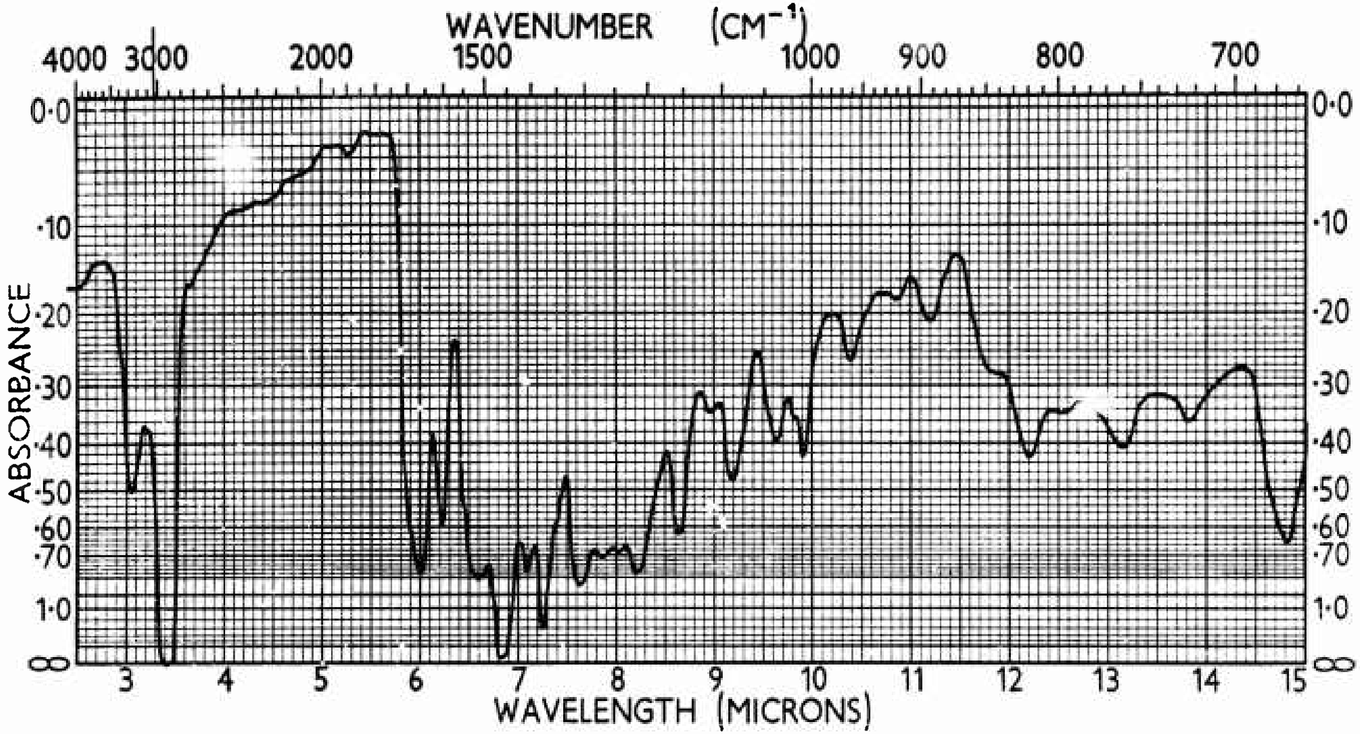


Figure 72. Infrared spectrum of bis[p-[N,N-(cis-2,3-butylene)ureido]benzyl]-N,N-(cis,2,3-butylene) ureido benzene (nujol)

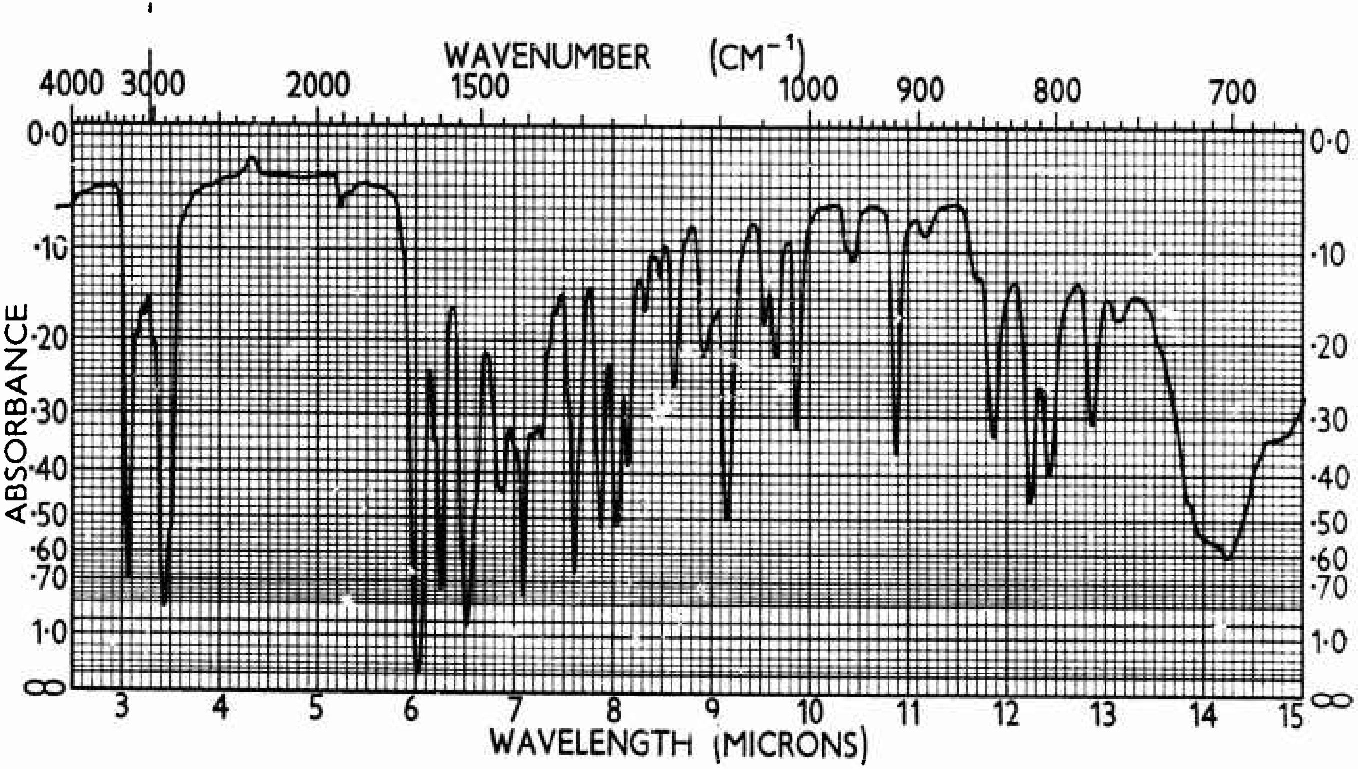


Figure 73. Infrared spectrum of bis[p-[N,N-(cis,2,3-butylene)ureido]phenyl]methane (nujol)

5. NMR Spectra of Reaction Products from N-Sulfonyl Aziridines with Carboxylic Acids

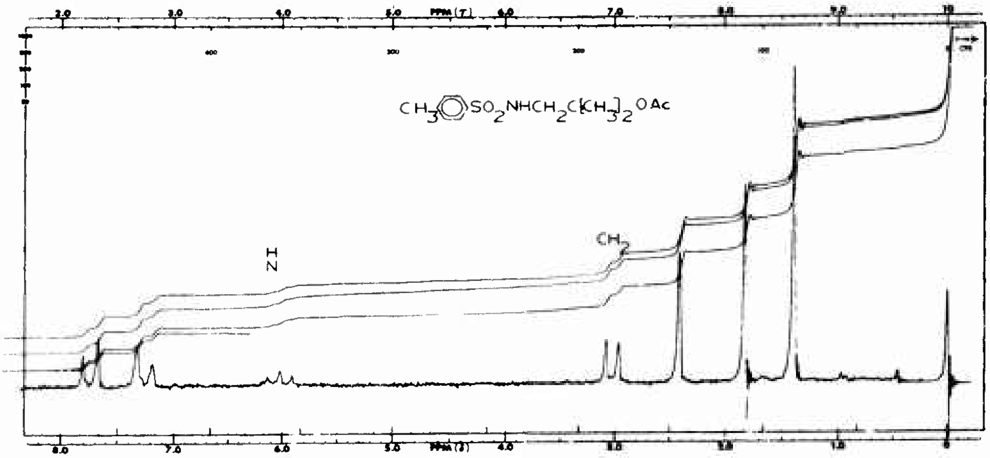


Figure 74. NMR spectrum of reaction product (IIb) from N-[p-methylphenylsulfonyl]-2,2-dimethyl aziridine with octanoic acid

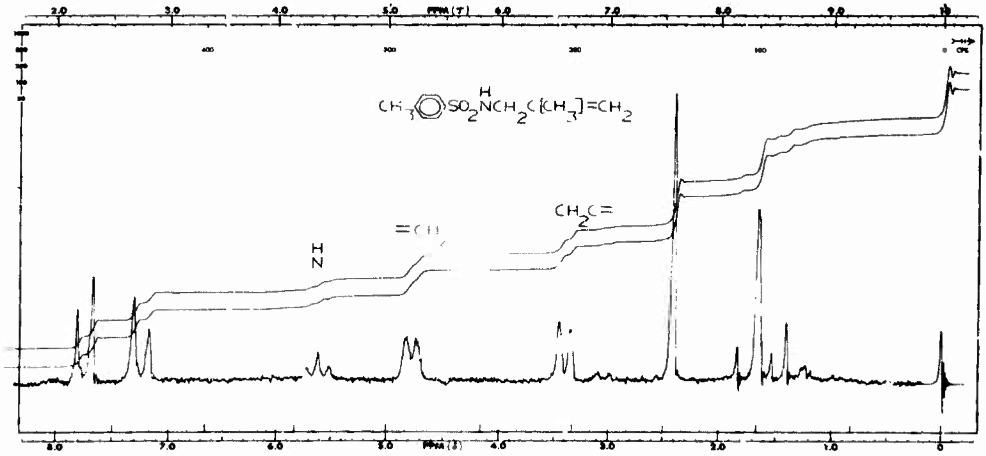


Figure 75. NMR spectrum of reaction product (IIIb) from N-[p-methylphenyl sulfonyl]-2,2-dimethyl aziridine with octanoic acid

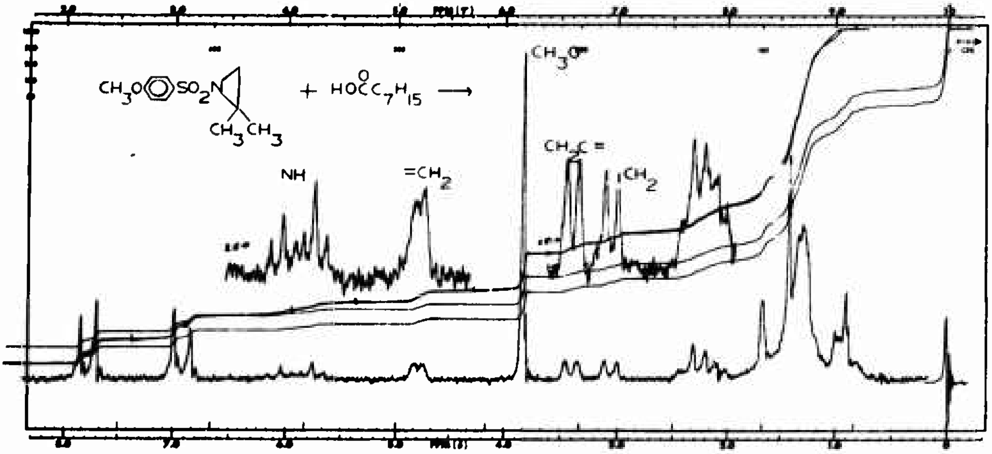


Figure 76. NMR spectrum of reaction products from N-[p-methoxyphenylsulfonyl]-2,2-dimethyl aziridine with octanoic acid

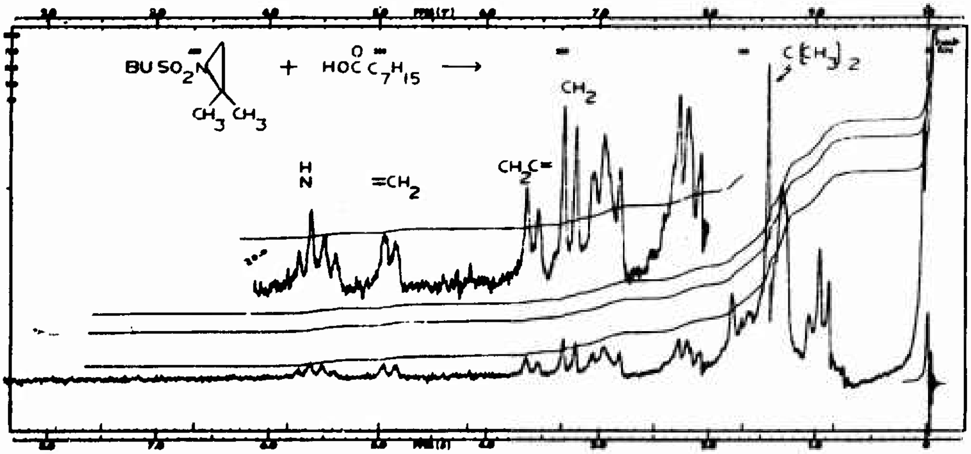


Figure 77. NMR spectrum of reaction products from N-[n-butyl sulfonyl] aziridine with octanoic acid.

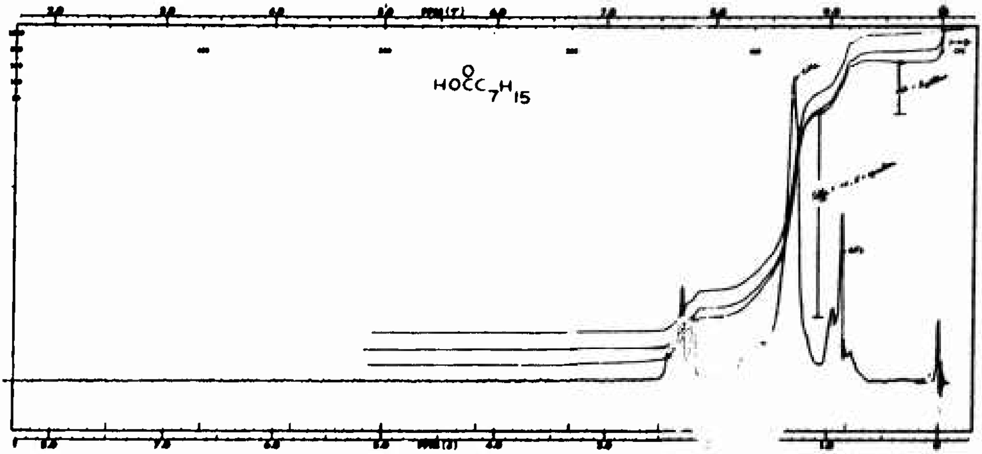


Figure 78. NMR spectrum of octanoic acid

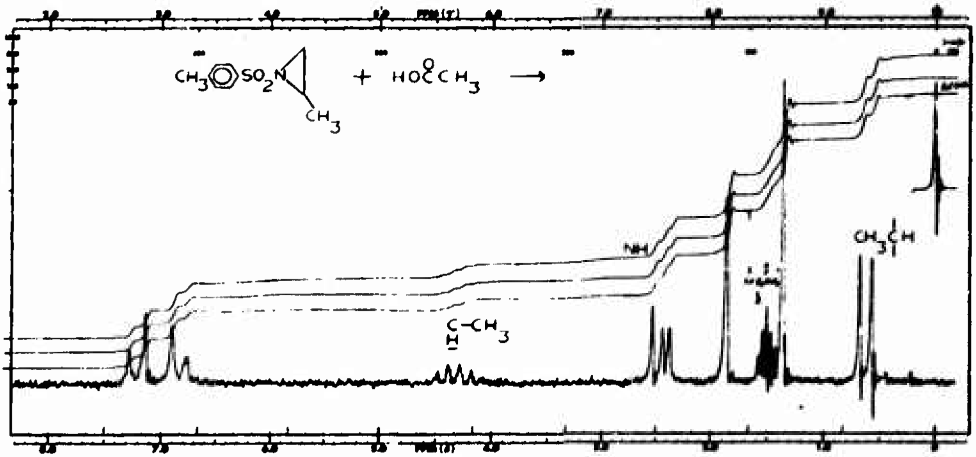


Figure 79. NMR spectrum of reaction products from N-[p-toluenesulfonyl]-2-methyl aziridine and acetic acid.

6. Infrared spectrum of p-bis-[cis-2,3-dimethyl aziridinyl]-tetra fluorobenzene

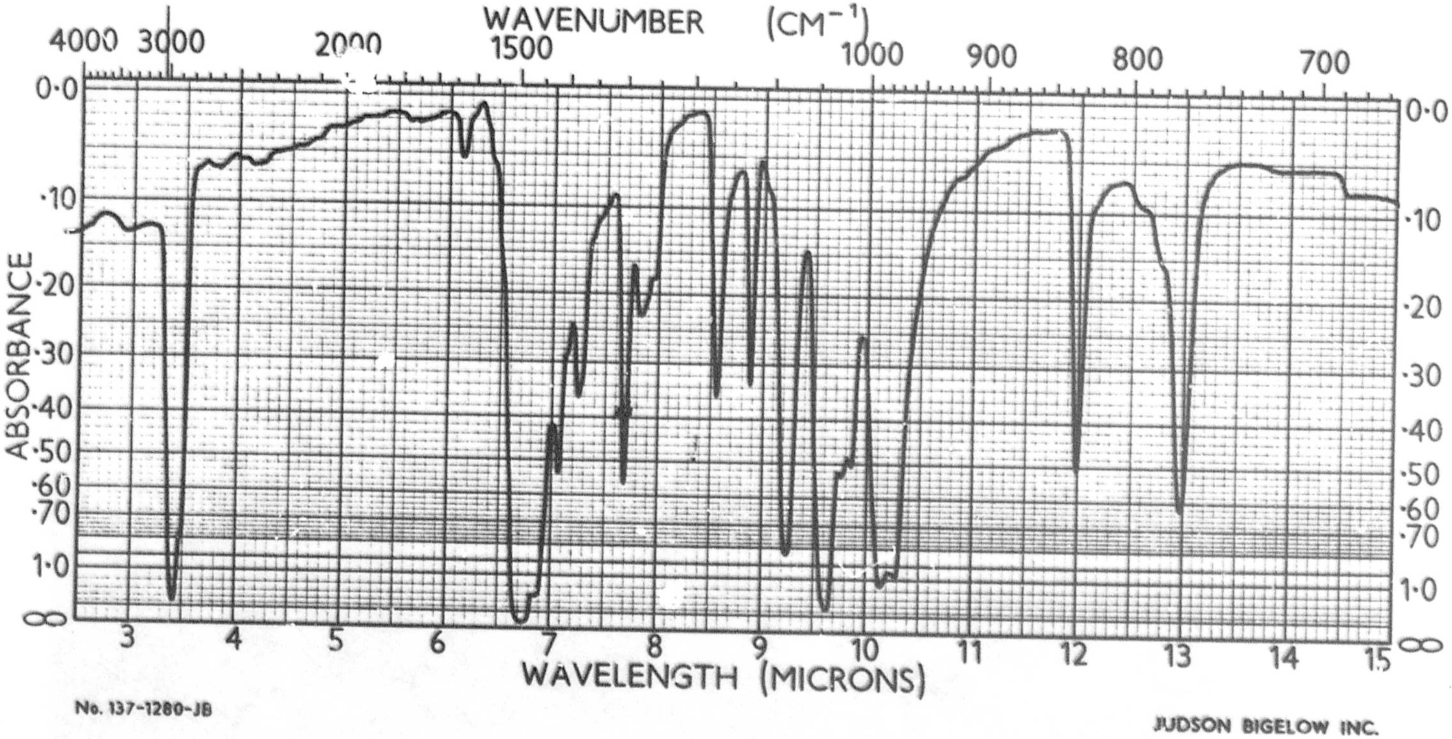


Figure 80. Infrared spectrum of p-bis-[cis-2,3-dimethyl aziridinyl]-tetra fluorobenzene

Unclassified

Security Classification

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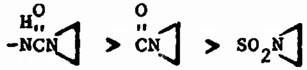
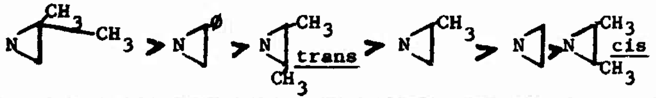
13. ABSTRACT

Curing agents for both carboxy and hydroxy-functional prepolymers have been investigated. A series of di- and trifunctional aziridines have been synthesized and evaluated. These include sulfonyl, acyl and ureido aziridines. Reactivity was found to decrease in the following order:



Reactivity and specificity of these aziridines is also affected by the substitution on the aziridine ring. The following order of decreasing reactivity was found:



The 2,3-dimethyl aziridines exhibit the highest degree of specificity. To get satisfactory cures with the sulfonyl aziridines a catalyst will be needed. Ureido and acyl 2,3-dimethyl aziridines give adequate cure rates at 150°F. The application of di/triisocyanate cure systems to hydroxy-terminated prepolymers has been limited in the past by the availability of commercial triisocyanates of acceptable purity. Two pure triisocyanates have been isolated from commercial sources and one of these has been evaluated in gumstocks. Mechanical properties

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

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13. Abstract (Cont'd)

of OH-Telagen-S gumstocks cured with di-/triisocyanates have shown that the maximum stress, initial modulus and Shore hardness is a function of diisocyanate structure and triisocyanate level whereas the maximum strain is solely dependent on the triisocyanate level. Aging studies of OH-Telagen-S gumstocks cured with di/triisocyanate have shown that the urethane cure linkage has adequate thermal stability at 275°F.

Unclassified

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Butarez CTL						
OH-Telagen-S						
Curing Agents						
Sulfonyl aziridines						
Acyl aziridines						
Ureido aziridines						
Monomethyl aziridines						
2,2-dimethyl aziridines						
cis-2,3-dimethyl aziridines						
trans-2,3-dimethyl aziridines						
reactivity						
specificity						
di- and triisocyanates						
mechanical properties of gumstocks at ambient temperatures and at 180°F						
HX-868						
Triphenyl dimethylene triisocyanate						
Triphenyl methane triisocyanate						
Aging of gumstocks						
Cure catalysts						

Unclassified

Security Classification