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HIGH ENERGY PROPELLANT INGREDIENT RESEARCH (U)

D.J. Mangold, T.C. Kraus, D.A. Csejka, J.A. Scruggs
OLIN MATHIESON CHEMICAL CORPORATION

Technical Report AFRPL-TR -66-94

May 1966

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FOREWORD

This report was prepared by Olin Mathieson Chemical Corporation, Chemicals Division, under Contract AF 04(611)-10548, Project 3148 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command. The work described in this report was conducted over the period 1 March 1965 through 28 February 1966 in the Olin Research Center, 275 Winchester Avenue, New Haven, Connecticut.

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Classified information has been extracted from asterisked documents listed under References.

The Technical Report has been reviewed and is approved.

George F. Babits, Lt. Colonel, USAF
Chief, Propellant Division

DISTRIBUTION

This report is distributed to the Chemical Propulsion Mailing List - March 1965 - Section I and Section II - 1, 2 and 3.

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ABSTRACT

The thermal stability of aluminum hydride (Olane 58) has been significantly improved by aging and water treatment. The effect is believed to be due to a surface coating of bayerite, $Al(OH)_3$. These treated samples demonstrated thermal stabilities of less than one per cent decomposition in the Taliani Test at 100°C for 8-12 hours or at 60°C for 50-75 days.

Studies of the synthesis of Olane 58 by the solid $LiAlH_4$ preparatory technique or through the addition of free radical inhibitors did not indicate the superiority of these modifications in present processes.

Direct crystallization of unsolvated aluminum hydride was demonstrated from a mixed toluene-ether solution.

Although the data from the Differential Scanning Calorimetry (DSC) scans both programmed and isothermal provide some insight into the thermal character of aluminum hydride, no meaningful correlations to Taliani Tests at 60°C and 100°C could be made for decomposition as low as one per cent.

Conductivity studies of the $LiAlH_4$-$AlCl_3$ reaction under a variety of conditions indicate the formation of a $AlH_3 \cdot 2LiAlH_4$ complex and chloroalane species.

PUBLICATION REVIEW

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I. INTRODUCTION

At the beginning of this program AlH_3 (Olane 58) could be routinely prepared in these laboratories with a thermal stability of less than one percent decomposition at 60°C in 20-30 days. This material could be synthesized by the addition of the free radical inhibitors 2-mercaptobenzothiazole (MBT) and phenothiazine (PTA) or by the solid $LiAlH_4$ synthesis technique.

The objective of this program was to prepare aluminum hydride of further improved thermal stability which would allow its use over extended time periods in solid propellant formulations. The approaches to this objective were:

- Achieve thermally stable AlH_3 through the use of additives and unique modes of preparation.
- Continue study of the fundamental nature of AlH_3 decomposition and phase conversion.

II. TECHNICAL APPROACH

A. Stabilization Through The Use of Inhibitors

1. Addition During Process

The results of earlier Differential Scanning Calorimetry studies (1) on Olane decomposition in air or oxygen suggested that the decomposition proceeded by a free radical route and therefore might be retarded by the use of conventional free radical inhibitors used in polymerization processes. A number of these were screened as potential candidates. Subsequent testing of Olane stability at 60° in the Taliani apparatus indicated that MBT (2-mercaptobenzothiazole), PTA (phenothiazine) and hydroquinone were effective in stablizing Olane 58 samples. The addition of sulfur caused no noticeable change. The aluminum hydrides which exhibited this improvement consisted of particles ranging in size from 30-70 microns; crude bulk densities were generally less than 0.5 g/cc.

One of the primary objectives of the present program therefore was to isolate large (and more dense) particles of Olane 58 by typical crystallization techniques and to improve their stability with the reagents previously tested.

In order to achieve this goal a high dilution process (6:1 toluene:ether) was investigated for the purpose of crystallizing unsolvated aluminum hydride from solution at elevated temperatures. The experimental details are given in the Appendix (Method B-2). Photos 1-4 show the initial precipitate (mixture of Olanes 60 and 58) and its gradual transformation to the final granular Olane 58 form at 95°C. The corresponding temperature profile is represented in Figure 1. This process was effective in producing glassy products, consisting mainly of dense crystalline agglomerates; but occasionally single crystals were detected in the 70-150 microns range at higher additive ratios of 0.35:1:0.35 ($LiAlH_4$:AlH_3:$LiBH_4$). In the initial

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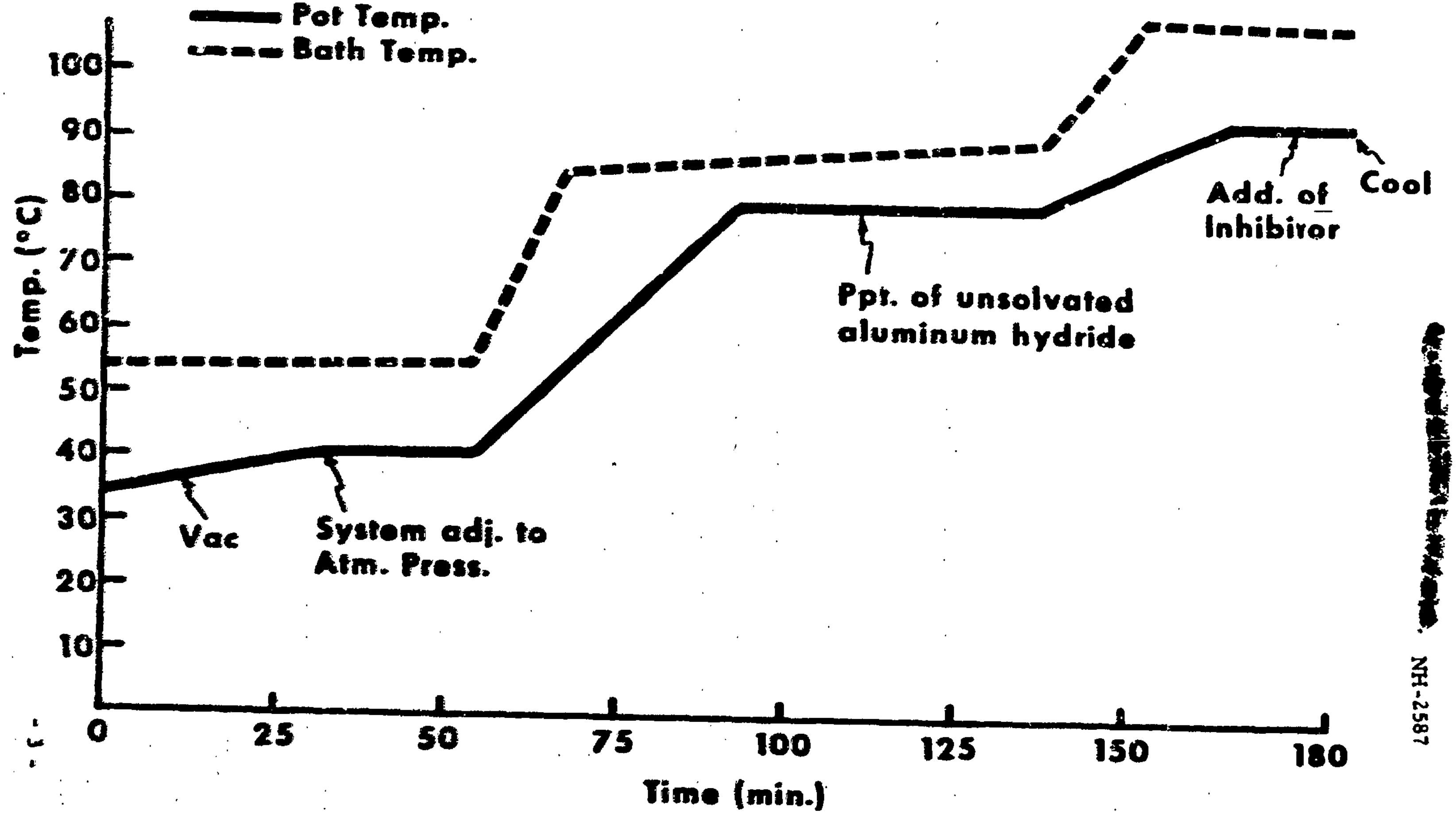
FIGURE 1
TIME-TEMPERATURE PROFILE OF HIGH DILUTION SYSTEM



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CRYSTAL GROWTH FROM ETHER-TOLUENE SOLUTION (80x)

PHOTO 1

PHOTO 2

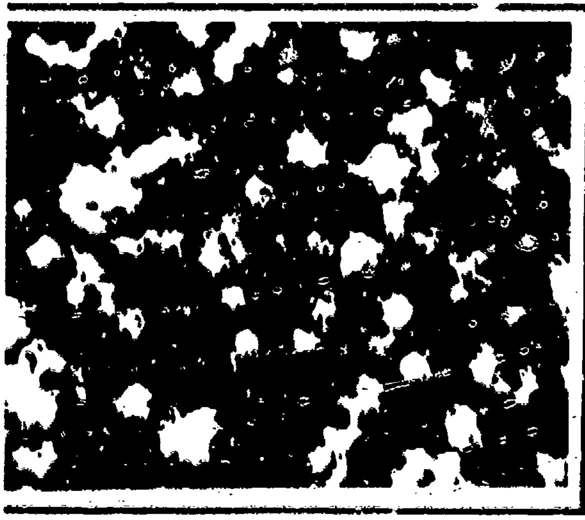

PHOTO 3

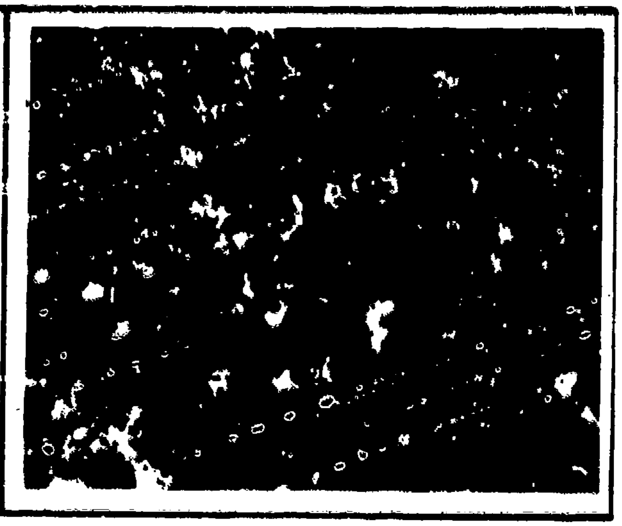

PHOTO 4

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stages of this study no inhibitors were included in order to establish controls. The results of the Taliani tests on the untreated particles are summarized in Table I. The lack of consistency in the thermal data indicate the difficulties in attempting to establish a standard thermal stability for these particles.

The results of thermal stability tests on samples which were treated with PTA and MBT are summarized in Table II. The concentration levels used were 0.04 g. and 0.2 g., respectively for 0.09 moles of aluminum hydride. It was confirmed that the ideal stage for addition of the inhibitors was during the conversion period at 95°. The initial investigations revealed that addition of the free radical inhibitors, particularly at the synthesis stage and below 90°C caused interference with the desolvation and conversion steps. A comparison of the data in Table I and II shows no major improvements in stability resulting from the addition of PTA and MBT. Typical stability curves are shown in Figure 2. It is possible that the greater specific area of the less dense Olane particles, prepared in the previous program (1) made these inhibitors more effective in their action.

Further comparisons of the stability of treated and untreated Olanes are summarized in Table III. In addition evaluations of several new additives of the amine type such as diphenylamine and urea were made. Two complex chelating agents, prepared in the Olin laboratories, with specificity for aluminum were also screened. A comparison of their stabilizing effect with the untreated samples showed no gross improvements in thermal stability.

The series of experiments represented by 1916D-21 in which $LiAlH_4$ and $LiBH_4$ were present during inhibitor addition and 1916D-22 (no LAH, LBH present) were performed to determine the degree of inhibitor consumption by the excess additives in solution and its subsequent effect on aluminum hydride stability. The results of this investigation were not conclusive, however, because of the excellent stabilities of the control

TABLE I

THERMAL STABILITIES OF HIGH DILUTION PRODUCTS - NO ADDITIVES

Expt. No.	Process	Additive Ratio LAH:AlH$_3$:LBH		Thermal Stability 60°C					
603673-13	6:1 (Tol:Et$_2$O)	0.23:1:0.17	Hr.	66	96	120			
			%. Dec.	.34	.61	.90			
603675-8	6:1 (Tol:Et$_2$O)	0.21:1:0.17	Hr.	67	96	120	168		
			%. Dec.	.41	.51	.60	.90		
607208-F	6:1 (Ben:Et$_2$O)	0.25:1:0.23(a)	Hr.	64	72	144	192		
			%. Dec.	.05	.08	.57	1.8		
603681-26B	6:1 (Tol:Et$_2$O)	0.23:1:0.17	Hr.	64	72	144	192	240	309
			%. Dec.	.05	.07	.14	.23	.47	1.2
1899-D-100	6:1 (Tol:Et$_2$O)	0.21:1:0.17	Hr.	88	120				
			%. Dec.	.49	1.43				
6074-63	6:1 (Tol:Et$_2$O)	0.21:1:0.17	Hr.	25	48	117	160	286	336
			%. Dec.	.10	.12	.16	.22	0.70	1.17

(a) Addition of solid LiAlH$_4$ in synthesis.
Additive ratio was probably greater due to premature precipitation of aluminum hydride.

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[illegible] MAL STABILITY OF [illegible]

Exp. No.	Inhibitor	Days	3	7	10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
			Thermal Stability Data							
1899D-98 (a)	None	°/. Dec.	0.10	0.23	0.30	1.4[illegible]	[illegible]	[illegible]		
6074-89	None	°/. Dec.	0.19	0.43	0.60	[illegible]	1.0			
6069-05 (b)	None	°/. Dec.	0.45	0.81	0.95	1.0(12 days)				
6074-92	None	°/. Dec.	0.25	0.43	0.55	[illegible]	0.85			
6074-79	None	°/. Dec.	0.25	0.65	1.32, + days					[illegible] sample
1916D-5 (a)	PTA	°/. Dec.	0.05	0.11	0.17	0.31	0.58	1.08		
1916D-6 (a)	MBT	°/. Dec.	0.39	1.3(6 days)						
1916D-12	MBT	°/. Dec.	0.38	2.12						
1916D-14 (c)	MBT	°/. Dec.	0.28	0.50	0.73	1.03(12 days)				
1899D-57 (d)	None	°/. Dec.	0.08	0.26	0.87	1.5(11 days)				
1899D-57A (e)	Water Vapor	°/. Dec.	0.03	0.12	0.23	0.56	1.20			
1916D-20	Sulphur	°/. Dec.	0.10	0.44	0.77	1.04(12 days)				
1916D-21 (f)	None	°/. Dec.	0.06	0.17	0.23	0.48	0.94(18 days)			
1916D-21A (g)	Diphenylamine	°/. Dec.	0.07	0.13	0.37	0.90	1.52(17 days)			
1916D-21B (g)	PTA	°/. Dec.	0.06	0.16	0.31	1.02(14 days)				
1916D-21C (g)	Urea	°/. Dec.	0.07	0.18	0.38	1.05(14 days)				
1916D-22 (f)	None	°/. Dec.	0.02	0.08	0.10	0.21	0.27			Leakage in system.
1916D-22A (h)	PTA	°/. Dec.	0.04	0.08	0.13	0.19	0.30			Leakage in system.
1916D-22B (h)	Urea	°/. Dec.	0.08	0.23	0.34	0.57	0.86	1.0(22 days		
1916D-22C (h)	Diphenylamine	°/. Dec.	0.03	0.09	0.16	0.27	0.43	0.60	0.81	1.0(33 days)
603690-23 (i)	None	°/. Dec.	0.11	0.34	0.66	1.0(12 days)				
603690-23	Complex Chelate no. 1 (j)	°/. Dec.	0.11	0.40	0.80	1.0(11 days)				Compare to 603690-23
603692-23 (i)	None	°/. Dec.	0.14	0.34	0.53	0.90	1.0(16 days)			
603692-23	Complex Chelate no. 2 (j)	°/. Dec.	0.10	0.30	0.55	1.1(14 days)				Compare to 603692-23

(a) Additive Ratio - 0.21 : 1.0 : 0.17 (LAH:AlH_3:LBH).
(b) Solid LAH Addition (99+%).
(c) 5 x MBT. Compare to 1916D-12.
(d) Solid LAH Addition (95+%). 2 : 1 Process. Additive ratio - (0.15 : 1.0 : 0.18).
(e) Compare to 1899D-57. 72 Hours H_2O vapor exposure.
(f) Control. 2 : 1 Process. Additive ratio - 0.15 : 1.0 : 0.18.
(g) Compare to 1916D-21. Inhibitor added in presence of LAH, LBH.
(h) Compare to 1916D-22. Inhibitor added in absence of LAH, LBH.
(i) Additive Ratio - 0.15 : 1.0 : 0.18.
(j) Prepared in Olin Laboratories.

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TABLE III

EFFECT OF INHIBITORS

Expt. No.	Additive Ratio LAH:AlH_3:LBH	Inhibitor		Thermal Stability 60°C						Bulk Density g./cc.
6074-63	0.21:1:0.17	None	Hr.	48	160	286	336			
			°/. Dec.	.12	.22	.70	1.17			
6074-65	0.21:1:0.17	PTA - 40°	Hr.	71	120	168				
			°/. Dec.	.23	.78	2.51				
6074-68	0.21:1:0.17	MBT - 40°	Hr.	71	97					
			°/. Dec.	.78	1.23					
6074-71	0.21:1:0.17	PTA - 95°	Hr.	67	192	264	328			0.62
			°/. Dec.	.07	.36	.68	1.18			>100 mesh
6074-74	0.21:1:0.17	MBT - 95°	Hr.	67	139	192				
			°/. Dec.	.16	.62	1.14				
6074-83	0.35:1:0.35	MBT - 95°	Hr.	26	184	242	262			0.71
			°/. Dec.	.06	.44	.83	1.05			>100 mesh
6074-86	0.35:1:0.35	PTA - 95°	Hr.	48	68	136				
			°/. Dec.	.52	.68	1.17				
1916D-10	0.35:1:0.35	PTA - 95°	Hr.	48	136	212	280	333		0.65
			°/. Dec.	.09	.16	.37	.65	1.06		
1916D-11	0.20:1:0.35	PTA - 95°	Hr.	21	88	141	184	259	311	
			°/. Dec.	.19	.35	.49	.55	.78	1.0	

samples, 1916D-21 (0.4%, 90 days, 60°) and 1916D-22 (0.54%, 90 days, 60°). Analyses of these samples disclosed loss of active hydrogen. Found: 9.2% (1916D-21) and 7.9% (1916D-22).

2. Post-Treatment With Additives

a. Contact Treatment

In this study small quantities of a sample, O-16 (-325 mesh), were treated with various reagents to determine their effect on thermal stability. A range of compounds were tested including amines, imines, alcohols as well as several free radical inhibitors. In these investigations the compound was dissolved in dry ether to give a solution of approximately 1 percent by weight. The Olane 58 (1-2 g.) was stirred in this solution for about one hour, filtered, and then dried. All operations were performed under nitrogen to avoid contamination from moisture. The Taliani stability data at 100°C are summarized in Table IV . For comparison of the 100°C and 60°C Taliani Tests see Task C. The better stabilities most noticeable in the tests which involved aqueous treatments e.g. siliclad. The later section concerned with water exposure, will show that the improvements can be related to the formation of a bayerite coating [$Al(OH)_3$] on the surface of the Olane 58. Slight improvements also resulted from contact with several free radical inhibitors such as 2,5-ditertiary butylhydroquinone and methoxybenzene.

b. Deposition Treatment

A series of compounds, primarily ethylenic, acetylenic, and heterocyclic listed in Table V were screened for their effectiveness in improving the thermal stability of Sample O-16 (-325 mesh). The Dow Chemical Co. (2) reported that diphenylacetylene had improved the thermal

TABLE IV

POST TREATMENTS OF OLANE 58 (SAMPLE O-16)*

		Percent Decomposition	
		100°C	Hours
	O-16	1.0	3.5
1.	1,3-Propanediamine	1.49	3.5
2.	1-Butyleneimine	1.10	3.5
3.	2,5-Ditertiarybutylhydroquinone	1.02	4.0
4.	p-Tertiarybutylphenol	0.9	3.5
5.	2,6-Ditertiarybutylphenol	>1.0	3.5
6.	Methoxybenzene	1.03	3.75
7.	6-Tertiarybutyl-*m*-cresol	0.8	4.0
8.	1-Amino-4-hydroxyanthraquinone	0.95	4.0
9.	"O-75" $C_8F_{16}O$	1.0	3.5
10.	"N-43" $C_{12}F_{27}N$	1.0	3.5
11.	Perfluorokerosene $C_{14}F_{30}$	1.0	3.5
12.	Glycerine (25 wt. %) in H_2O	1.05	4.5
13.	Glycerine (25 wt. % in water) followed by Siliclad (10 vol. % in water)	(Sample not tested because of poor results of tests no. 12 and 14.)	
14.	Siliclad (10 vol. %) in H_2O	1.0	4.3
15.	Siliclad (10 vol. %) in H_2O and water wash	1.22	6.0
16.	Collodion (1.0 wt. %) in C_2H_5OH	1.18	4.0
17.	Water Wash and Collodion Treatment	Dec. of prod.	
18.	Sodium Aluminate in water	*	
19.	Water treatment (long term)	*	
20.	2,5-Ditertiarybutylhydroquinone	1.0	3.5
21.	Diethylamine	1.0	3.0
22.	Glycerine (5.50 wt. % H_2O)	(Discarded sample. Could not remove glycerine completely)	
23.	Siliclad (5.0 wt. % H_2O)	2.0	3.5
24.	Toluene Diisocyanate	>1.0	3.5
25.	Di-orthotolylcarbodiimide	1.0	2.75
26.	Butyl isocyanate	1.5	4.0
27.	Ag from Rochelle salt solutions	1.0	3.75
28.	Methylene blue water solution	1.0	6.5

* No Bayerite detected

TABLE V

POST-TREATMENTS OF OLANE 58

		Hydrocarbon Weight Per Cent	Hrs. 100°C-1°/. Dec.
	Sample O-16		3.5
1.)	Methylphenylacetylene	2.8	3.5
2.)	1-Phenyl-1-butyne	2.3	3.5
3.)	Diphenylacetylene	7.9	4.5
4.)	5-Decyne	1.9	3.5
5.)	4-Octyne	5.0	4.0
6.)	1-Hexyne	3.9	3.5
7.)	Allylbenzene	5.7	4.0
8.)	3-Butyne-2-ol	6.1	4.0
9.)	Methylphenylacetylene	9.9	4.0
10.)	N-Ethylmorpholine	6.1	3.5
11.)	3-Butyn-2-ol	20.5	4.0
12.)	Allylbenzene	22.0	4.0
13.)	Methylphenylacetylene	22.5	3.5
14.)	Diallylmelamine	2.72	4.5
15.)	Diallylamine	1.62	4.0
16.)	1,5-Pentanediol (98°/.)	4.99	4.0
17.)	Hexyleneglycol	1.88	4.5
18.)	Isoquinoline	3.10	4.0
19.)	3-Picoline (98°/.)	2.24	4.0
	Sample O-17		3.0
20.)	1-Methylcyclohexene	3.32	3.0
21.)	Diethylacetylenedicarbamate	2.05	3.0
22.)	1,8-Nonadiyne	1.99	3.0
23.)	2,4-Dimethylthiazole	3.75	3.0
24.)	Hexamethyldisiloxane	1.90	2.5-3.0
25.)	2-Methyl-5-ethylpyridine	2.11	2.5-3.0
26.)	Benzylsulfoxide	3.41	3.0

stability of their aluminum hydride. Our method consisted of slurring the Olane sample in an ether solution of the various additives, then evaporating the ether, and thereby depositing a residue of the additive on the aluminum hydride. Slight improvements in stability were observed for several compounds, namely diallylmelamine, hexylene glycol, and diphenylacetylene. Although it was recognized that the high concentrations of additives would contribute to a large excess of carbon , it was of interest, nevertheless, to determine whether more of the additive (20. 5 - 22. 5 percent) would cause improved stability. A comparison of allyl benzene at various concentration levels (5. 7 and 22. 0 percent) indicated that this was not the case.

c. Miscellaneous Treatments

The results of several acid-base post-treatments are illustrated in Table VI . None of the treatments, however, produced any greater improvement than that obtained from a simple aqueous wash.

3. Treatments with Water

Investigations at the Hercules Powder Company(3) on aluminum hydride surfaces has shown that the major differences between aluminum hydride samples, particularly with respect to thermal stability, processability, and compatibility may be due to variations in surface properties. Their findings, based on neutron activation analysis, indicated oxygen contents of 0. 34 to 2. 9°/。 for a number of samples. Additional data from VPC measurements revealed that water, either absorbed on the surface or part of a hydrated alumina structure, varied from 0. 02 to 0. 28°/。. The treatment of aluminum hydride samples with deuterium oxide gave evidence that products with virgin surfaces reacted readily to yield hydrogen deuteride, whereas those which yielded less HD had surfaces which were contaminated with oxygen or absorbed water. Their interpretation of these results was

TABLE VI

POST TREATMENTS OF OLANE 58 (SAMPLE O-16)

		Percent Decomposition	
		100°C	Hours
	O-16	1.0	3.5
1.	H_2O - HCl* (pH ~ 2.0)	1.0	5.5
2.	H_2O - $NaOH$** (pH ~ 10.0)	1.0	6.5
3.	H_2O - H_3PO_4 (pH ~ 2.0)	1.0	5.0
4.	H_2O - NH_4OH (pH ~ 10.0)	1.0	4.5
5.	H_2O - HNO_3 (pH ~ 2.0)	1.0	4.5
6.	H_2SO_4 (conc.)	1.0	3.75

* No Bayerite detected.

** Bayerite detected on surface of Olane 58.

that the more highly oxidized surfaces presented a greater barrier to penetration by D_2O molecules and subsequent reaction with aluminum hydride.

Powder analysis of aged (1 - 2.5 yr.) Olane 58 samples in the Olin laboratories disclosed the presence of bayerite (beta alumina trihydrate) in varying quantities on a number of these. Thermal testing of "aged" Olane 58 samples also showed that several of these exhibited improved stability. However, not all "aged" samples of improved stability contained bayerite, but the evidence was sufficiently strong to suggest that a material with a surface deactivated by moisture would be characterized by better thermal stability.

These findings led to a study of surface deactivation by water and the subsequent effect on thermal stability. Table VII and Figure 3 summarizes investigations with Olane 58 samples from various sources. Three techniques for "hydrating" the Olane surface were employed, namely: 1) water vapor exposure in a closed system, 2) a 2-3 minute water slurry treatment and 3) a 30-minute steam treatment.

a. Water Vapor

In this treatment the Olane was spread over the surface of a course sintered-glass funnel which is joined to an Erlenmeyer flask partially filled with water. This system was closed and then held at room or other desired temperatures for several days. The loosely bound water was then removed under vacuum prior to thermal testing of the sample.

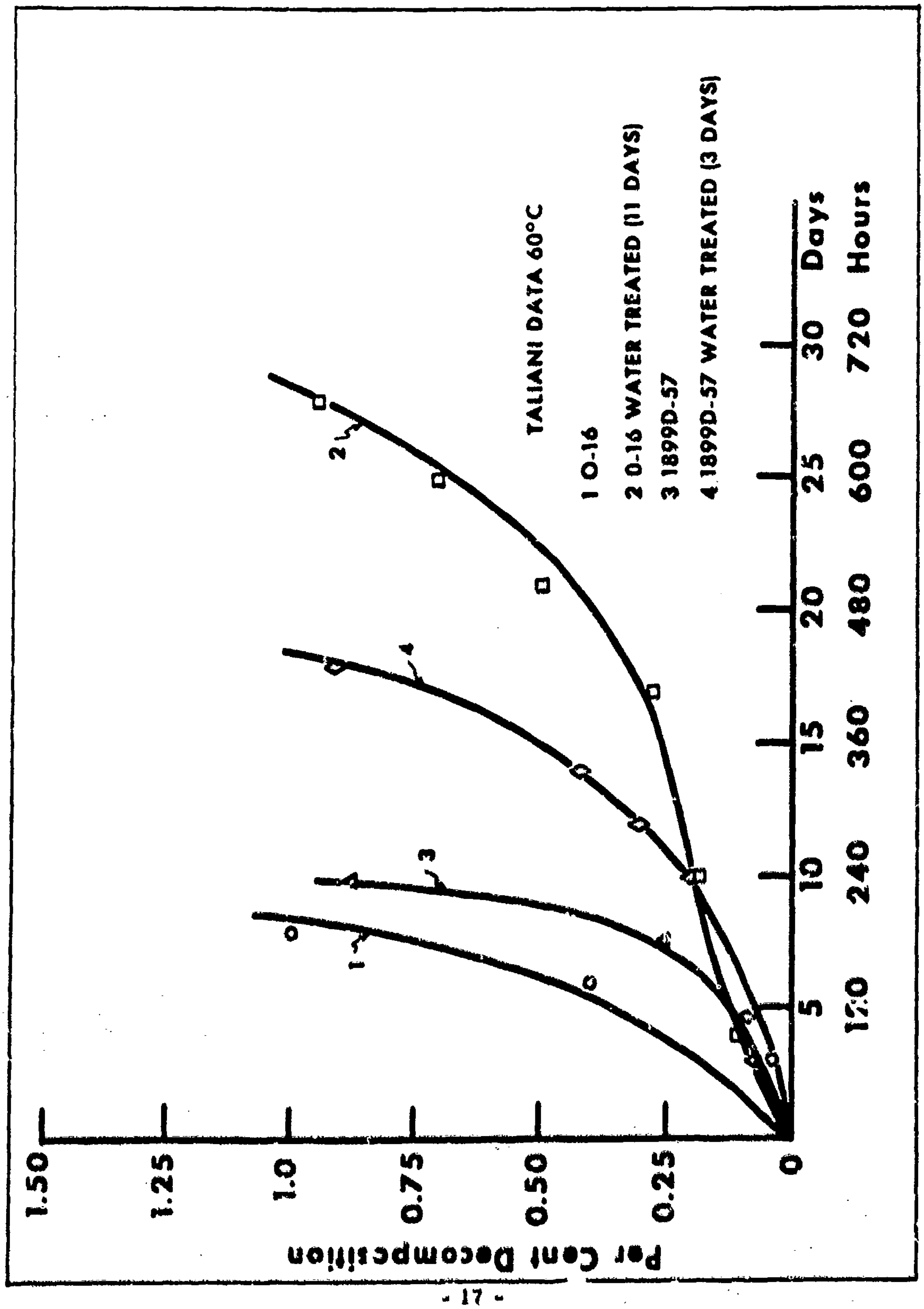
b. Slurry

The Olane sample in small quantities was added to water cooled to 0-5° and slurried for 2-3 minutes. After filtration, the sample was washed several times with ether and then dried on a high vacuum system

TABLE VII

EFFECT OF MOISTURE (TALIANI, 1% DECOMPOSITION)

SAMPLE NO.	ORIGINAL TALIANI 60°	ORIGINAL TALIANI 100°	TYPE OF WATER TREATMENT	RESULTANT THERMAL STABILITY 60°	RESULTANT THERMAL STABILITY 100°	COMMENTS
1899D-57	11 days		3 day - vapor	18 days		
O-16	8 days	3.5 hr.	11 day - vapor	28 days	5.75 hr.	
O-16	"	"	Water slurry 0-5°	30 days	6.5 hr.	Active H = 9.3%
O-16	"	"	11 day - vapor - heated 45° - 2.5 hr.		6.2 hr.	Active H = 9.3%
606632-12		4.0 hr.	11 day - vapor		6.75 hr.	
602521A		~10.25 hr.	11 day - vapor		7.5 hr.	
1899D-12		~12.0 hr.	11 day - vapor		8.0 hr.	
607258A		3.8 hr.	Water slurry 0-5°		0.34% - 6.0 hr.	Loss of active hydrogen from 8.6 to 6.5% due to presence of micro-crystalline particles.
602566A		4.25 hr.	Steam - 30 min.		—	Loss of active hydrogen from 9.4 to 5.7% - presence of appreciable bayerite.
O-16			Decomposed at 100° to 0.4% (2.5 hr.) - then moisture treated for 6 days		~2.0 hr.	
602568A	—	—	Water slurry 0-5°		12.5 hr.	No change from 2.5 yr. aged sample.



EFFECT OF WATER VAPOR TREATMENT

Fig. 3

at room temperature.

c. Steam

Steam was generated in a flask. Then a small sample of Olane in a carrier constructed of a modified course-sintered glass funnel was suspended inside the flask and exposed for 30 minutes. A final vacuum drying procedure was again employed.

All of the above treatments tend to form beta alumina trihydrate on Olanes possessing a virgin surface. The treatments with the exception of the steam exposure improved the thermal stability with less than 5 per cent loss in active hydrogen. The latter technique caused extensive degradation of the aluminum hydride. An analysis of the residue indicated only 5.7% active hydrogen. Appreciable bayerite was detected by X-ray on the residual Olane instead of the expected alpha alumina monohydrate, boehmite.

The data show that several aged samples with excellent thermal stability were not improved by the water exposure techniques. The reasons for this are not obvious, but it is possible that extended heating at 100° dehydrates some of the bayerite, and the resulting free water is then available for reaction.

Most samples showed a slight loss of active hydrogen after a water treatment. In the case of a partially microcrystalline sample such as 607258A, loss of active hydrogen was appreciable, especially from the direct water wash.

4. Sample Aging

The initial evidence that long term storage might improve thermal stability came from Sample 605589, a product prepared by the solid $LiAlH_4$ route. Its original thermal stability was 31 days at 60° before exceeding one percent decomposition. This characterized it as the most stable sample tested up to that time. After more than a 1 yr. - residence at room temperature in a brown sample bottle and under a nitrogen blanket an improvement, corresponding to 52 days at 60°, was observed. Analyses indicated no loss of active hydrogen. X-ray examination did not show the presence of bayerite.

The monitoring of various samples brought to light some further interesting findings. Three samples prepared in our Pilot Plant and stored at -20°C for over one year exhibited no change in stability, even though traces of bayerite were detected on a least one sample. Several "aged" samples prepared from $NaAlH_4$ showed improved stability; one did not. Samples C-9-2 and S-114, both mercury treated products stored at room temperature were found to be less stable. A summary of the data is shown in Table VIII and illustrated in Figures 4 and 5.

The present evidence indicates that colder temperatures apparently prevent changes in thermal stability. This suggests that a number of phenomenon may be occurring either singly or simultaneously at room temperatures over longer time periods. The more obvious of these are:

a) Slow conversion of trace quantities of unstable polymorphs to Olane 58.

b) A slow surface reaction with oxygen or moisture.

c) Further polymerization of the Olane 58 form - cross linking elimination of crystal defects, cavities, etc.

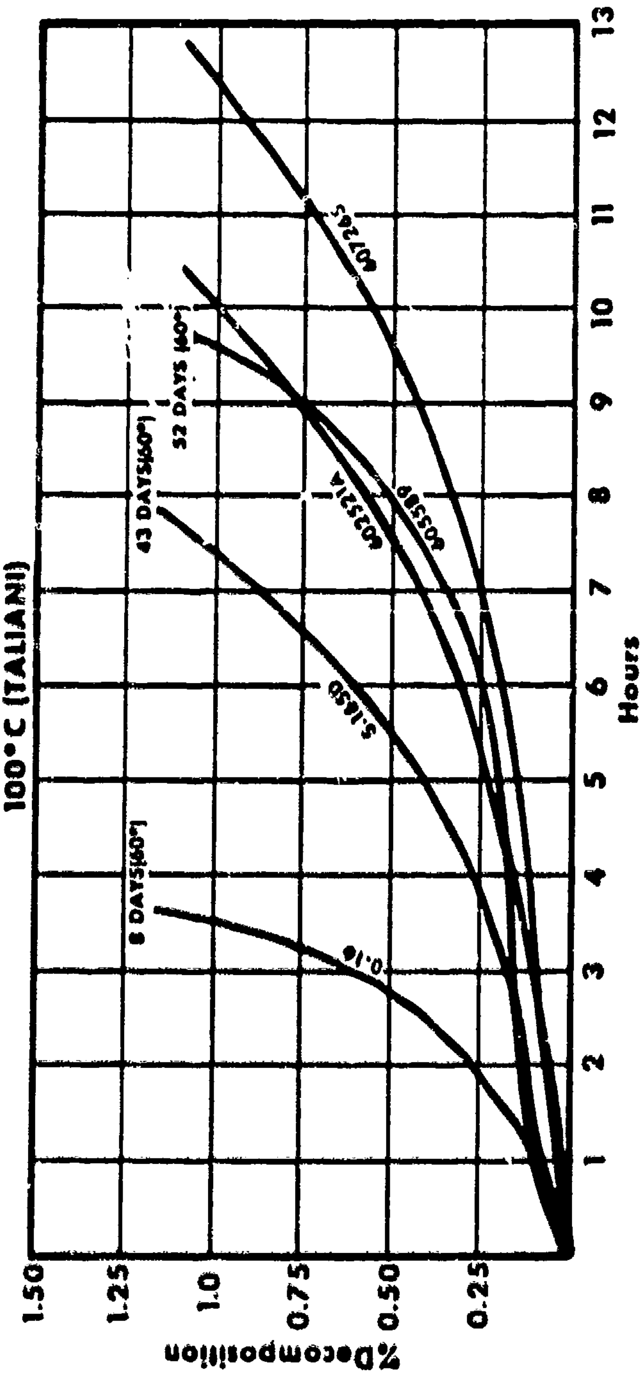
A study was initiated to simulate the effects of long term storage by "curing" a variety of samples at 40-45° under conditions otherwise similar to those for the aged samples. Periodic checks of their thermal stability and active hydrogen content were made. The results of this investigation is summarized in Table IX . Under the conditions tested, no improvements were apparent.

TABLE VIII

EFFECT OF AGING (1 % DEC.)

SAMPLE NO.	SAMPLE HISTORY	ORIGINAL T.S.	CURRENT T.S.	CURRENT X-RAY
605589	Solid $LiAlH_4$ - 1.5 yr. r.t.	31 days - 60°	52 days - 60° 8.5 hr. - 100°	No bayerite.
O-16	Pilot plant - 1.3 yr. (-20°C)	8 days - 60°	No change	Trace bayerite.
8-165D	Pilot plant - 2 yr. r.t.	41 days - 60°	43 days - 60° 50 hr. - 80° 7.5 hr. - 100°	Bayerite.
602521A	$NaAlH_4$ product - 2.5 yr. r.t.	4 hr. - 100° - 2.3%	10.25 hr. [illegible]	No bayerite.
1899D-12	Solid $LiAlH_4$ + MBT additive - 1 yr. r.t.	—	~12 hr. - 100°	No bayerite.
C-92	Pilot plant - mercury treated 2 yr. r.t.	4 hr. - 100° - 0.22%	4 hr. - 100° - 0.36% 6.5 hr. - 100° - 1.1%	
S-114	Pilot plant - mercury treated 2 yr. r.t.	4 hr. - 100° - 0.38%	3.75 hr.	
602558A	$NaAlH_4$ product - 2.5 yr. r.t.	—	2.5 hr. - 100° [illegible].19%, 60°, 26 days	No bayerite. Mass spec. analysis showed presence of high m. w. hydrocarb[illegible]
602566A	$NaAlH_4$ product	—	6.4 hr. - 100°	No bayerite.

Figure 4
EFFECT OF AGING
100°C (TALIANI)



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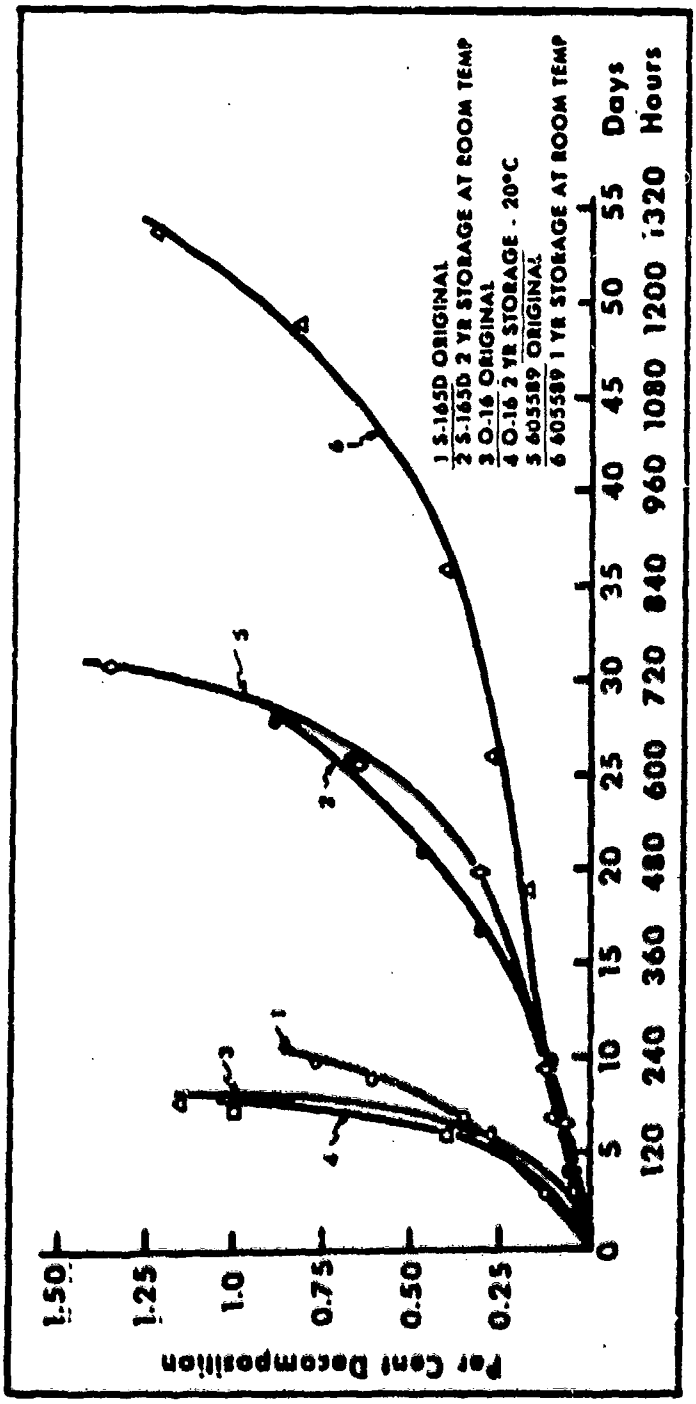


EFFECT OF AGING - TALIANI DATA 60°C

Fig. 5

TABLE IX

TALIANI DECOMPOSITION DATA (100°C)

AGING AT 40-43°C

Sample No.	Original Stability	14 Days	18 Days	20 Days	24 Days	41 Days	42 Days	48 Days	72 Days
606632+35 (606632-12) (606635-25)	– 1.2% - 4.5 hrs. 1.2% - 5.75 hrs.	1.2% - 6.5 hrs.						1.15% 6 hrs.	
606648-25	1.10% in 5 hrs.		1.10% 5 hrs.				1.33% 5 hrs.		
606649-25	1.02% in 5.75 hrs.		1.10% 5.75 hrs.				1.02% 5.25 hrs.		
606650-25	0.97% in 8 hrs.		0.237% 6 hrs.			0.95% 8.5 hrs.			
606652-20	1.06% in 10 hrs.	0.271% 6.5 hrs.			0.272% 7 hrs.			0.342% 6 hrs.	0.408% 6 hrs.
606655-23	.98% in 5 hrs.			1.0% 3.25 hrs.					

B. Stabilization Through the Use of Different Preparatory Techniques

The $NaAlH_4$-$AlCl_3$ process produced samples in the past of macrocrystalline Olane 58 which, without the benefit of any subsequent treatment, exhibited at that time unusually good thermal stabilities. The reasons for this are not well understood, but there are some obvious differences from the conventional $LiAlH_4$-$AlCl_3$ synthesis route. These are based primarily on the insolubility of $NaAlH_4$ in ether. In the $NaAlH_4$ route no prior polymerization of the AlH_4^- is possible. Furthermore, the AlH_3 is synthesized in the presence of a large excess of $AlCl_3$. The mechanism postulated has predicted intermediates of $HAlCl_2$, and H_2AlCl which infrared results appear to confirm.(4) These differences prompted the study of some variations in the preparative technique for Olane 58 based on the $LiAlH_4$-$AlCl_3$ reaction system. They were: (a) slow addition of solid $LiAlH_4$ to an $AlCl_3$- ether solution, and (b) simultaneous addition of reactants involving little or no excess of either reactant. The products of both variations have shown significant improvement in thermal stability.(1) Many parameters of AlH_3 processes have been shown to affect the thermal stability of AlH_3. The objective of this task, therefore, was to investigate those parameters which are applicable to the two preparative techniques. The specific approaches undertaken are presented.

It is reasonable to assume that more nearly perfect and purer crystals of Olane 58 should have an improved stability. However, it is also possible that the impurities and additives in the Olane actually contribute a stablizing effect. An additional objective of this task was therefore to isolate single crystals of Olane 58 and firmly establish the thermal stability of this product.

In the normal crystallizations studies investigated in the past, Olane 60 is precipitated and subsequently converted to Olane 58 which is in the form of agglomerated crystals. Since Olane 60 is known to be slightly soluble in ether, the conversion probably involves dissolving of Olane 60 and precipitation of Olane 58 as well as solid-solid conversion.

During the conversion some single crystals of Olane 58 appear to form as indicated by microscopic examination. These crystals then agglomerate. The fact that the formation of Olane 58 can take place by two different routes is probably not conducive to single crystal formation. It has been indicated that Olane 58 can be obtained from very dilute solutions containing Olane 60 as well as from solid Olane 60 in the well known "dry process". It is reasonable to assume that both of these transformations could take place in a continuous process. Since it is believed that the solid-solid transformation in the process must be avoided if the more perfect crystal is to be formed, investigations were made using very dilute solutions of aluminum hydride.

1. Solid Addition

In order to determine the reasons for the improved thermal stability of aluminum hydride as prepared by the solid $LiAlH_4$ process, investigations were conducted using both the crude $LiAlH_4$ (95^+ percent) and purified $LiAlH_4$ (99^+ percent). Typical reaction procedures are described in the Appendix (Method A). The results of these experiments are presented in Table X. The products of these reactions were compared on several bases:

(a) physical crystal character

(b) crude bulk density and

(c) thermal stability at 100°C

The crude bulk densities ranged from 0.4 g/cc. to 0.7 g/cc. with no preference shown for any preparatory procedure. All products were crystalline aggerates of similar appearance.

In normal practice, all ether used in washing products is distilled from $LiAlH_4$. This procedure was found to be very important to

TABLE X

COMPARISON OF OLANE 58 FROM DIFFERENT REACTION CONDITIONS

Expt. No.	Reaction Type	Toluene to Ether Ratio	Excess Additives LAH	LBH	Final Product Crude Bulk Density	Active Hydrogen	Thermal Stability 100°C % Dec.	Hrs.
606631	Pure Solid Addition	2:1	20	18	.40	9.4	1 %	4.5
606633	Solution Solution	3:1	20	18	-	9.4	1 %	5.0
606635	Pure Solid Addition	2:1	20	18	-	9.4	1.25 %	5.75
606639	Crude Solid Addition	2:1	20	18	.37	9.0	1.10 %	4.75
606640	Pure Solid Addition	2:1	20	18	.40	-	1.67 % 80°C	26
606641	Crude Solid Addition	2:1	20	18	.54	-	1.1 % 80°C	42.75
606643	Crude Solid Addition	2:1	20	18	-	-	1.83 %	3.0
606644	Solution Solution	3:1	20	18	.71	9.5	0.76 %	4.0
606645	Crude Solid Addition	3:1	20	18	.56	9.5	1.04 %	5.75
606648	Crude Solid Addition	2:1	40	18	.55	9.8	0.95 %	5.0
606649	Crude Solid Addition	3:1	20	18	.61	9.6	1.28 %	6.0
606650	Crude Solid Addition	2:1	20	18	.44	9.7	1.04 %	8.0(a)
606651	Crude Solid Addition	2:1	20	18	.62	9.6	1.21 %	9.5(a)
606652	Solution Solution	2:1	20	18	.55	9.4	1.06 %	10.0(a)
606654	Crude Solid Addition	3:1	20	18	.37	-	1.26 %	6.0(b)
606655	Solution Solution	2:1	20	18	.42	9.5	1.07 %	9.0(b)

(a) Washed with ether containing 0.45% H_2O.

(b) This sample was washed with ether containing 14 p.p.m. H_2O.

the apparent stability of the final product. It can be seen from the results, that when care is taken to use dry ether (14-100 ppm. H_2O) in washing Olane 58, one percent decomposition occurs in 4-5. 5 hours at 100°C. However, washing with wet ether improves this stability to the extent where 8-10 hours becomes the rule. A more complete investigation of wet ether washing is described in other sections of this report. On the basis of these results it is possible to conclude that the thermal stability of the Olane 58 is independent of the initial reaction synthesis procedure.

2. Direct Crystallizations

a. Dilute Solutions

Investigations of diluta solutions with the 1:6 ether-toluene Olane laboratory process have been concerned with the effects of several parameters on the crystal shape, size and thermal stability of the final Olane 58.

A series of temperatures from 60 to 85°C for crystallising Olane 58 directly from solution was screened. A number of experiments performed at 60°C resulted in final products which were usually a mixture of polymorphs Olanes 57, 60 and 58. Considerable decomposition was also observed in several experiments. It is interesting to note that investigations at the 60°C temperature produced unusually large particles in several experiments both hexagonally shaped rods and spheres of Olane 60 but conversion of these materials to Olane 58 resulted in crystal fissures. (See Photos 5 and 6).

Further investigations were conducted at 65°, 70°, 75°, 80° and 85°C. The better products, essentially granular Olane 58, were obtained at 75°C (5 hours) and 80°C (2 hours) even though the latter conditions appeared to produce crystals fairly rapidly. The bulk density of the final

PHOTO 5
OLANE 60
80x

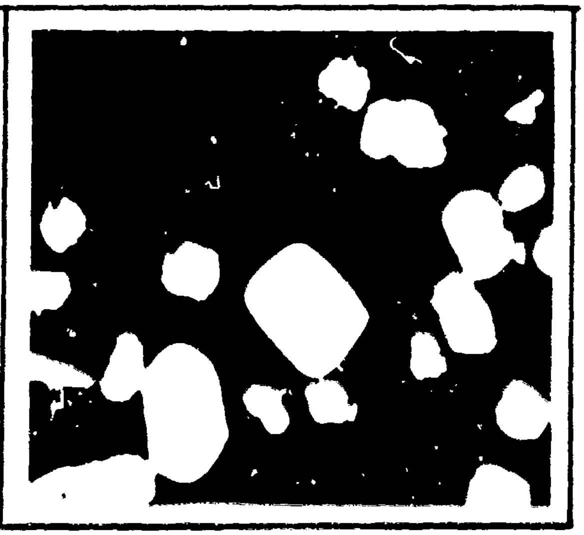


PHOTO 6
OLANE 58
80x

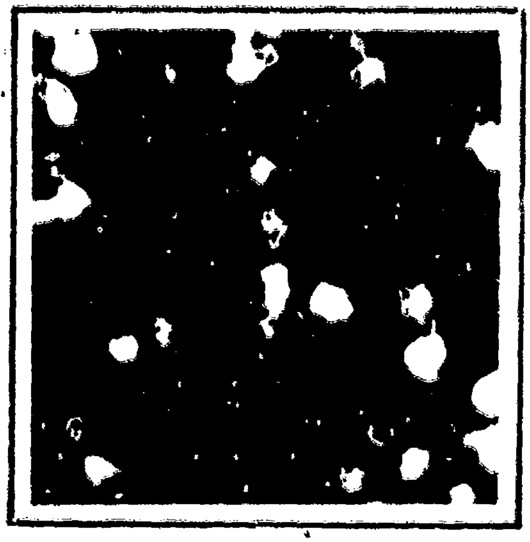


PHOTO 7
OLANE 58
75°C DIRECT CRYSTALLIZATION
80x

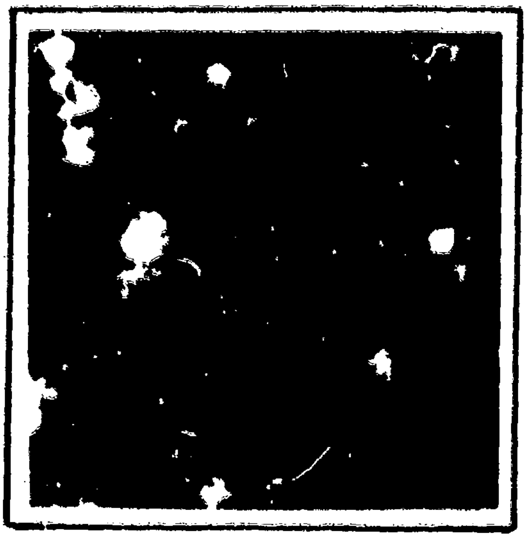


PHOTO 8
OLANE 58
80°C DIRECT CRYSTALLIZATION
80x

65 to 0.82 g/c.c. (See Photos 7 and 8).
ndix (Method B).
eriment in which the ether content at
ntly stopped at ~8% ether and then
the initial product contained large cubes,
rs at 75°C yielded spherical Olane 57.

and shape of the particles from the
d, the thermal stability of these products
esult in the past from the addition of
preparatory technique. Table XI
cerned with direct crystallization of

olutions

tallize unsolvated Olane directly from
yield of product, experiments were
evel using a 3:1 toluene:ether ratio.
Olane 60 and or 58 directly out of this
e ether content before raising the
to the crystallization temperature
ils see Appendix (Method C).
roducts prepared with this procedure
and 606633. The crude bulk densities
/cc. which is comparable to products
ecomposition of 1 percent was observed

the results of these experiments.

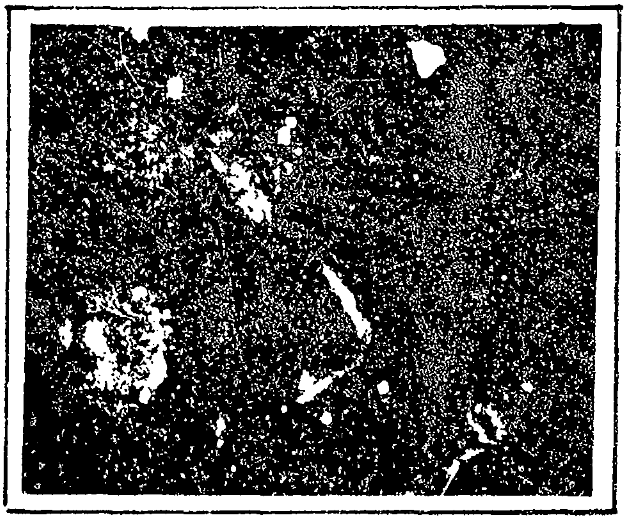


PHOTO 9
INITIAL PRECIPITATE
80x

PHOTO 10
FINAL PRODUCT
PRIMARILY OLANE 57
80x

TABLE XI

DIRECT CRYSTALLIZATION

Exp. No.	Additive Ratio LAH:AlH$_3$:LBH	Temp. °C	Time (hr.)	Initial Ppt. Time	Final Product X-ray	Remarks
6074-89	0.35:1:0.35	80 95	.75 .3	-	O-58 Some amorph.	
6074-92	0.35:1:0.35	95	.3	-	O-58 Some amorph.	
6074-94	0.35:1:0.35	80	2.0	-	O-58 Some O-60, tr. Al	
6074-99	0.35:1:0.35	85-87	2.5	-	O-58, tr. L. Cl	Initial Ppt. O-60
603694	0.15:1:0.18	65	21.0	1 hr.	O-58, some 57 tr. O-60	
603688	0.15:1:0.18	70	20.0	6 hr.	-	
603692	0.15:1:0.18	75	5.0	at 71°	O-58	
603696	0.15:1:0.18	75	5.0	2 hr.	O-58	
603690	0.15:1:0.16	80	2.0	0:3 hr.	O-58 tr. O-60	

TABLE XII

EVALUATION OF CONDITIONS FOR 3:1 DIRECT CRYSTALLIZATION

Expt. No.	Conc. AlH_3 in Et_2O(M/L)	Mole Percent Additives		First Crystals			Final Product		
		LAH	LBH	Temp.	% Et_2O	X-Ray	X-Ray	Bulk Density	Thermal Stability
606610	25	15	18	60°C	4.5-5%	Olane 62	58	.71	-
606612	25	15	18	75°C	7-8%		57	.33	-
606614	25	15	18	72°C	5.5-6%		58 trace 60	.56	-
606616	25	15	18	60°C	4.5-5%		58	.63	0.8% 7 days, 60°C
606618	25	15	18	60°C	5-6%	Olane 62	58	.61	-
606620	25	20	18	80°C	6-7%	Olane 60	58	-	-
606623	25	20	18	80°C	6-7%	15% 58 Olane 60	58	.66	-
606628	25	20	18	89°C	6-7%	12% 58 Olane 60	58	.60	1.12% 2.5hrs., 100°C

c. Mixed Hydrocarbon Solvents

A crystallization media of benzene, toluene and ether was investigated to determine the possibility of growing more singular crystals by taking advantage of the better solubility of AlH_3 in benzene-ether mixtures. In these mixtures, also, a higher temperature could be attained for crystallization over that of a benzene-ether mixture. In the mixed hydrocarbon-ether system it is possible to approach the ideal condition for a slow precipitation of the unsolvated Olane which appears as singular crystals, but the final product isolated is an agglomerated material. The results of these experiments are presented in Table XIII. For experimental details see Appendix (Method D). The thermal stability of these aggregates was slightly lower than Olane 58 previously isolated from the toluene ether system. This slight difference can probably be attributed to the difficulty in washing large aggregates which can encapsulate $LiAlH_4$ and other fine or lesser thermal stability.

The mixed hydrocarbon technique was also coupled with another approach for direct crystallization of Olane. Earlier studies had shown this effect through the use of little or no excess of $LiAlH_4$ and the presence of $Al(BH_4)_3$. A general procedure is desribed in the Appendix (Method E). This technique did offer better solubility properties but in the 3:1 hydrocarbon-ether system the final product was again large aggregates. It also showed a unique property of growing round crystalline aggregates of Olane 58. The thermal stability of the products were significantly lower than that of product isolated by other methods.

The results of these experiments are presented in Table XIV.

3. Effect of Wet Ether

After it was discovered in other experiments (Table X)

TABLE XIII

INVESTIGATION OF THE MIXED HYDROCARBON SYSTEM

Expt. No.	Diluent to Et_2O Ratio	Mole Percent Excess LAH	Mole Percent Excess LBH	H_2O Content of Wash Et_2O	C	H	X-Ray	Bulk Density	Active Hydrogen	Thermal Stability 100°C %. Dec.	Thermal Stability 100°C Hours
*606670	3:1	11	18	14-100 p. p. m.	-	-	58	.45	9.8	1.72%.	5
*606670	3:1	11	18	14-100 p. p. m. then .45%.	-	-	58	-	9.4	1.04%.	11
*606671	3:1	11	18	14-100 p. p. m.	-	-	58 Same 60	-	-	-	-
*606671	3:1	11	18	14-100 p. p. m. then .45%.	-	-	-	-	-	-	-
*606674	3:1	35	35	14-100 p. p. m.	-	-	58	.70	-	1.34%.	4
*606674	3:1	35	35	14-100 p. p. m. then .45%.	.6	9.7	58	-	9.2	0.49%.	6
*606676	3:1	35	35	14-100 p. p. m.	.4	9.9	58	.58	-	1.0%.	3
*606678	4:1	35	35	14-100 p. p. m.	-	-	58	.59	-	1.15%.	3
*606678	4:1	35	35	14-100 p. p. m. then .45%.	.5	9.9	58	-	-	1.0%.	5
*606679	3:1	35	35	14-100 p. p. m.	.4	9.6	58	-	-	1.09%.	4.5
*606679	3:1	35	35	14-100 p. p. m. then .45%.	-	-	58	-	-	0.491%.	7
*606682	6:1	35	35	14-100 p. p. m. then .45%.	.8	10.0	58	.66	-	1.24%.	6

* All products were split and one part washed with wet ether for comparison with portion washed with dry ether.

TABLE XIV

INVESTIGATIONS USING $Al(BH_4)_3$

Expt. No.	Benzene-Toluene Ether Ratio	Mole Percent Excess $LiAlH_4$	$LiBH_4$	$Al(BH_4)_3$*	Final Product Analysis	100°C Thermal Stability °/. Dec.	Hours
606680	1.5:1.5:1	None	35	37	Olane 62		
606681	1.5:1.5:1	(17)**	35	6	Olane 58	0.8	2
606683	1.5:1.5:1	(17)**	35	8	Olane 58	1.0	3

* Estimated.

** $LiAlH_4$ added at 80-85°C.

that water in the wash ether makes a critical difference in the thermal stability of the final product, experiments were designed in this task to evaluate the effect of wet ether. Products were prepared through the various synthesis routes, divided into several portions and washed with ether of different water concentrations. The thermal stability of these products were compared with standard untreated products from the same reaction. Table XV presents the results of these experiments.

In the crude product (before washing) a mixture of Olane, $LiAlH_4$ and $LiBH_4$ are present. Therefore, three types of wash treatments were employed. These were (1) washing with ultra dry ether, (2) washing with a combination of dry and then wet ether, and (3) washing with wet ether only. A vigorous reaction was observed in the third case along with the formation of apprecialbe non-separable "fines".

On the basis of these studies it is evident that the $LiAlH_4$ level is critical. In the presence of water this reagent will probably form LiOH which may then react further with the virgin surface of the freshly formed aluminum hydride. From the results of the foregoing experiments, however, it is clear that the moisture content of the ether, employed for washing final aluminum hydride products, is an important factor in improving the thermal stability.

TABLE XV

COMPARISON OF PRODUCTS WASHED WITH WET AND DRY ETHER

Expt. No.	Reaction Type	Toluene Ether Ratio	Excess		Water Content of the Wash Ether	X-Ray	PRODUCT		Thermal Stability	Remarks
			LAH	LBH			Bulk Density	Active Hydrogen		
** 606657	Solid Crude	2:1	20	18	.024%	58	.41	9.8	1.17% 5 hrs.	**This product was split into three parts 506657^1 and 606657^2.
606657^1	Solid Crude	2:1	20	18	0.24%, then .18%	58	.43	8.9	8.25 hrs.	Washed first with Et_2O with 0.024% H_2O, then with ether with .18% H_2O.
606657^2	Solid Crude	2:1	20	18	.18%	58	-	6.1	-	Washed with ether with .18% H_2O.
** 606660	Solid Crude Addition	2:1	20	18	79-98 p.p.m.	58	.42	9.5	1.07% 4 hrs.	**This product was split into two parts.
** 606660	Solid Crude	2:1	20	18	.18%	58	-	8.0	0.962% 4 hrs.	Washed with Wet Et_2O only.
606662	Solid Crude	2:1	20	18	14-100 p.p.m.	58 tr 60	.30	9.5	1.0% 4.0 hrs.	
606662	Solid Crude	2:1	20	18	14-100 p.p.m. then .5%	58 tr 60	-	9.1	1.0% 8.25 hrs.	
605662	Solid Crude	2:1	20	18	.5%	58 tr 60	-		-	Separation from the LAH and LBH hydrolysis products could not be achieved.
* 606665	Solution Solution	3:1	11	18	14-100 p.p.m.	58	.55	9.9	1.0% 3.5 hrs.	
* 606665	Solution Solution	3:1	11	18	14-100 p.p. then .45%	58	-	9.6	0.398% 6 hrs.	
* 606667	Solution Solution	3:1	11	18	14-100 p.p.m.	58	.46		1.47% 4.5 hrs.	
* 606667	Solution Solution	3:1	11	18	14-100 p.p.m. then .45%	58	-		.29% 7 hrs.	
* 606668	Solution Solution	3:1	11	18	14-100 p.p.m.	58	.60	9.7	1.54% 5 hrs.	
* 606668	Solution Solution	3:1	11	18	14-100 p.p.m. then .45%	58	-	9.4	1.01% 10.25 hrs.	
* 606673	Solution Solution	3:1	35	35	14-100 p.p.m.	58	.72		1.1% 4 hrs.	
* 606673	Solution Solution	3:1	35	35	14-100 p.p.m. then .45 H_2O	58	-	9.5	0.67% 6 hrs.	

* All products were split and one part washed with wet ether for comparison with standard which was washed with dry ether.

4. Conductometric Studies

The objective of this task was to study the syntheses of aluminum hydride by conductometric techniques and thereby determine the appearance or removal of ionic species during reaction which may effect the properties of Olane 58. The experimental details of these studies are presented in the Appendix.

Figure 6 is a composite of several experiments showing the specific conductance vs. the mole ratio of $LiAlH_4$ to $AlCl_3$. The reason for the variable mole ratio scale is merely to illustrate the typical conductance changes occuring over the entire mole ratio range as $LiAlH_4$ and $AlCl_3$ solutions are mixed. Although these results were obtained using ether-toluene solutions, the shape of the curve is typical for all solvent systems used in this study.

Evans, Kennedy and Del Greco (5) have conducted similar investigations concerning the reactions of $LiAlH_4$ and $AlCl_3$ in anhydrous ether. Their results indicate that a sharp maximum in the conductivity occurs at 17% of the equivalent amount of $LiAlH_4^*$ ($LiAlH_4/AlCl_3 = 0.51$) when $LiAlH_4$ is added to $AlCl_3$. Our results for the same process show that a maximum is attained at a mole ratio of approximately 0.34 as seen in Figure 7. Likewise Evans *et al.* obtained a maximum at 20-50% of equivalence ($LiAlH_4/AlCl_3 = 15-7$) when $AlCl_3$ was added to $LiAlH_4$. The results from our investigations show a maximum occurs at a ratio of $LiAlH_4/AlCl_3 = 11.0$. If the assumption is made that the reaction goes to completion after each increment is added, then it is possible to obtain the mole ratios of $AlCl_3/AlH_3$ or $LiAlH_4/AlH_3$ depending on which reactant is still in excess. Thus, when $AlCl_3$ is in excess after added $LiAlH_4$

$$AlCl_3/AlH_3 = \frac{3 - LiAlH_4/AlCl_3}{4\left(\frac{LiAlH_4}{AlCl_3}\right)},$$

---

* Equivalence is calculated according to the reaction $AlCl_3 + 3LiAlH_4 \longrightarrow 4AlH_3 + 3LiCl$

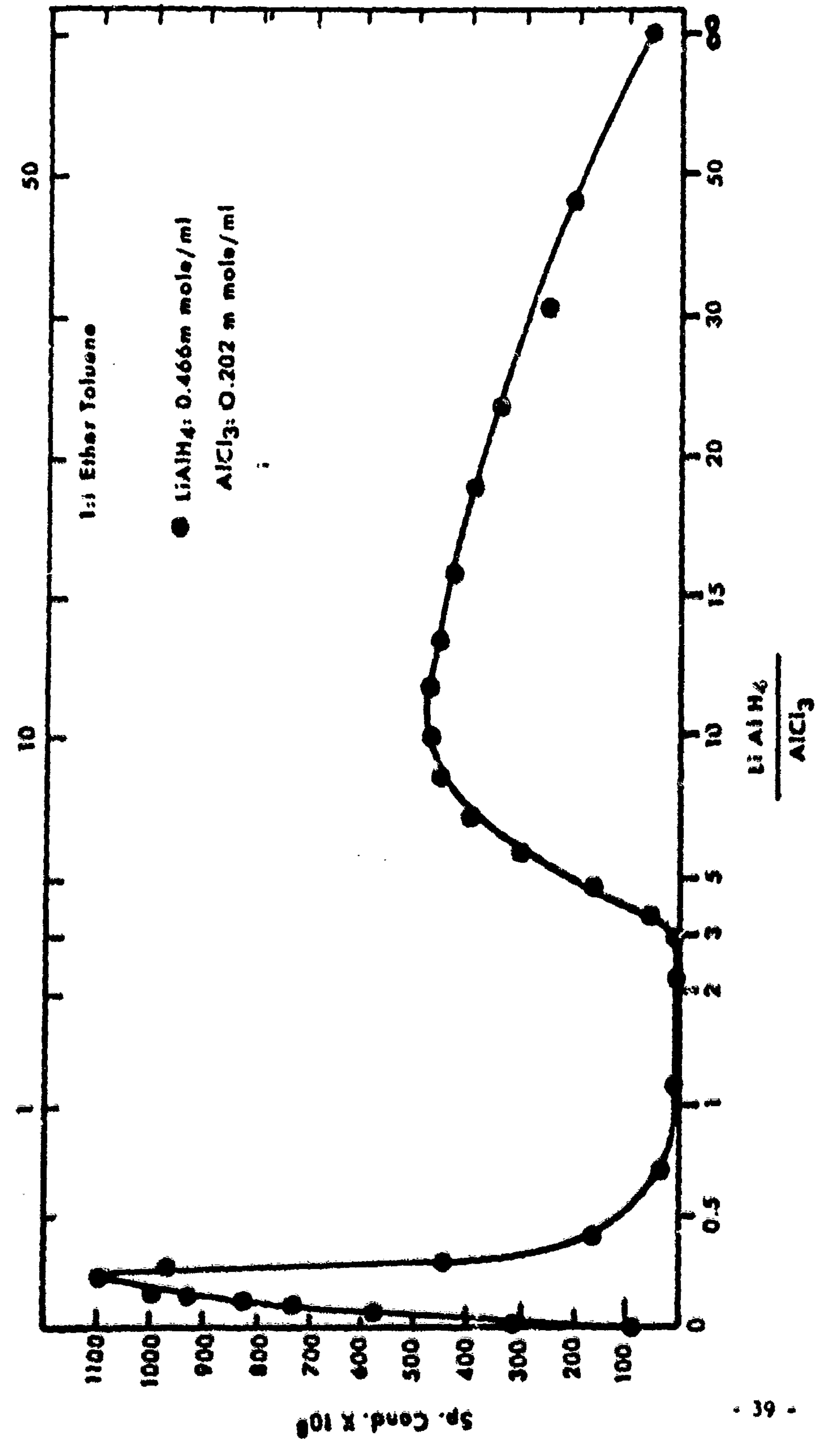


Figure 6
$LiAlH_4$-$AlCl_3$ TITRATION AT 25°C

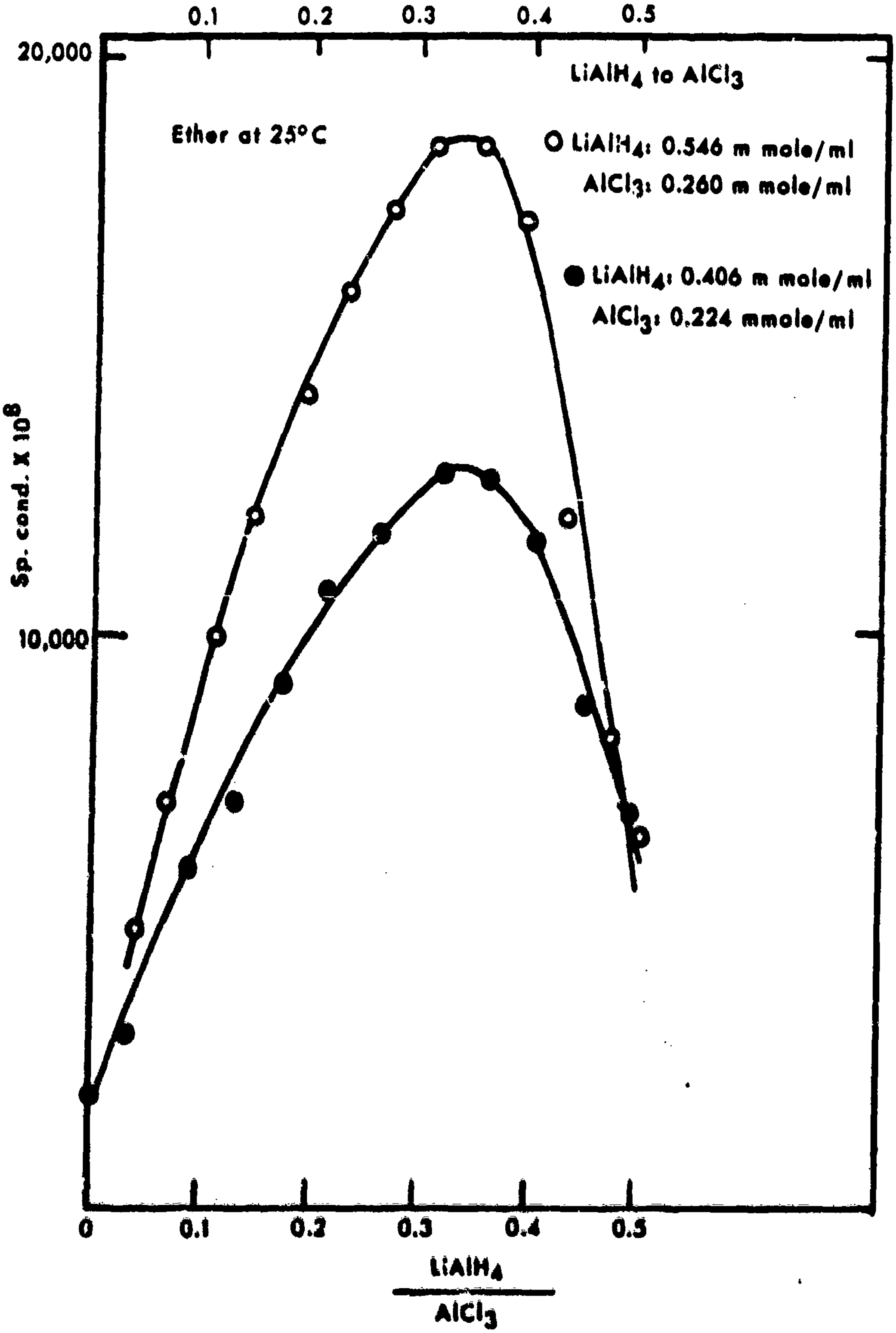


Figure 7
ADDITION OF LiAlH$_4$ TO AlCl$_3$ IN ETHER

and when $LiAlH_4$ is in excess

$$LiAlH_4/AlH_3 = \frac{\left(LiAlH_4/AlCl_3 - 3\right)}{4}.$$

Figure 8 shows the results of the addition of $AlCl_3$ to $LiAlH_4$. The maximum at $LiAlH_4/AlH_3 = 2.0$ corresponds to the ratio of $LiAlH_4/AlCl_3 = 11.0$.

The titrations were also carried out with mixed solvents. Figure 9 shows the results of the addition of $LiAlH_4$ to $AlCl_3$ where both reactants are dissolved in equal volume mixtures of ether-toluene and ether-benzene. At 25°C in ether-toluene the maximum is obtained at a ratio of $LiAlH_4/AlCl_3 = 0.22$, while at 50° it is shifted to approximately 0.17. The maximum in ether-benzene at 25°C is near 0.19. When the reverse titration was attempted, i.e., the addition of $AlCl_3$ to $LiAlH_4$ so that the equivalence point is passed and excess $AlCl_3$ is continually added, no maximum was obtained. This is in agreement with the findings of Evans and co-workers.

Figures 10 and 11 represent the results of the titrations in ether-toluene and ether-benzene solutions when $LiAlH_4$ is in excess. It should be noted that the maximum at a ratio of 2.0 for $LiAlH_4/AlH_3$ is obtained independent of the mode of mixing the reactants. That is, it made no difference whether (1) $AlCl_3$ was added to $LiAlH_4$, (2) $LiAlH_4$ was added to $AlCl_3$ so that the equivalent point of the reaction was reached and excess $LiAlH_4$ resulted, or (3) the previous solution was back titrated with $AlCl_3$.

The lithium chloride precipitate in all the above titrations was allowed to remain in the cell during the measurements. To examine the effects of the lithium chloride, equivalent amounts of $LiAlH_4$ and $AlCl_3$ were mixed, allowed to stand for approximately ten minutes and then filtered. The solution was transfered to the cell and $AlCl_3$ was added. The specific conductivities were less, but similar to the experiments having the LiCl

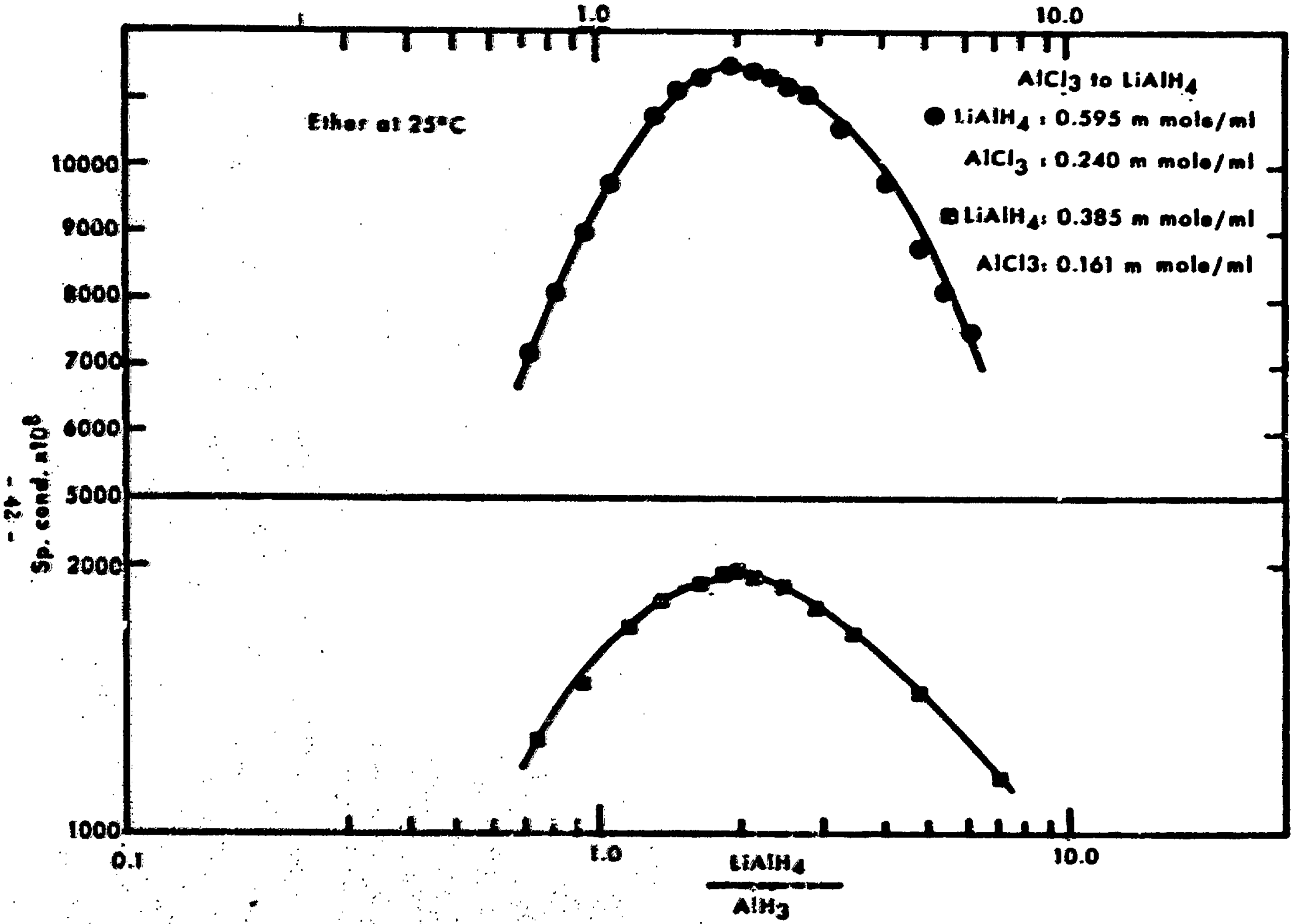


Figure 8

ADDITION OF $AlCl_3$ TO $LiAlH_4$ IN ETHER

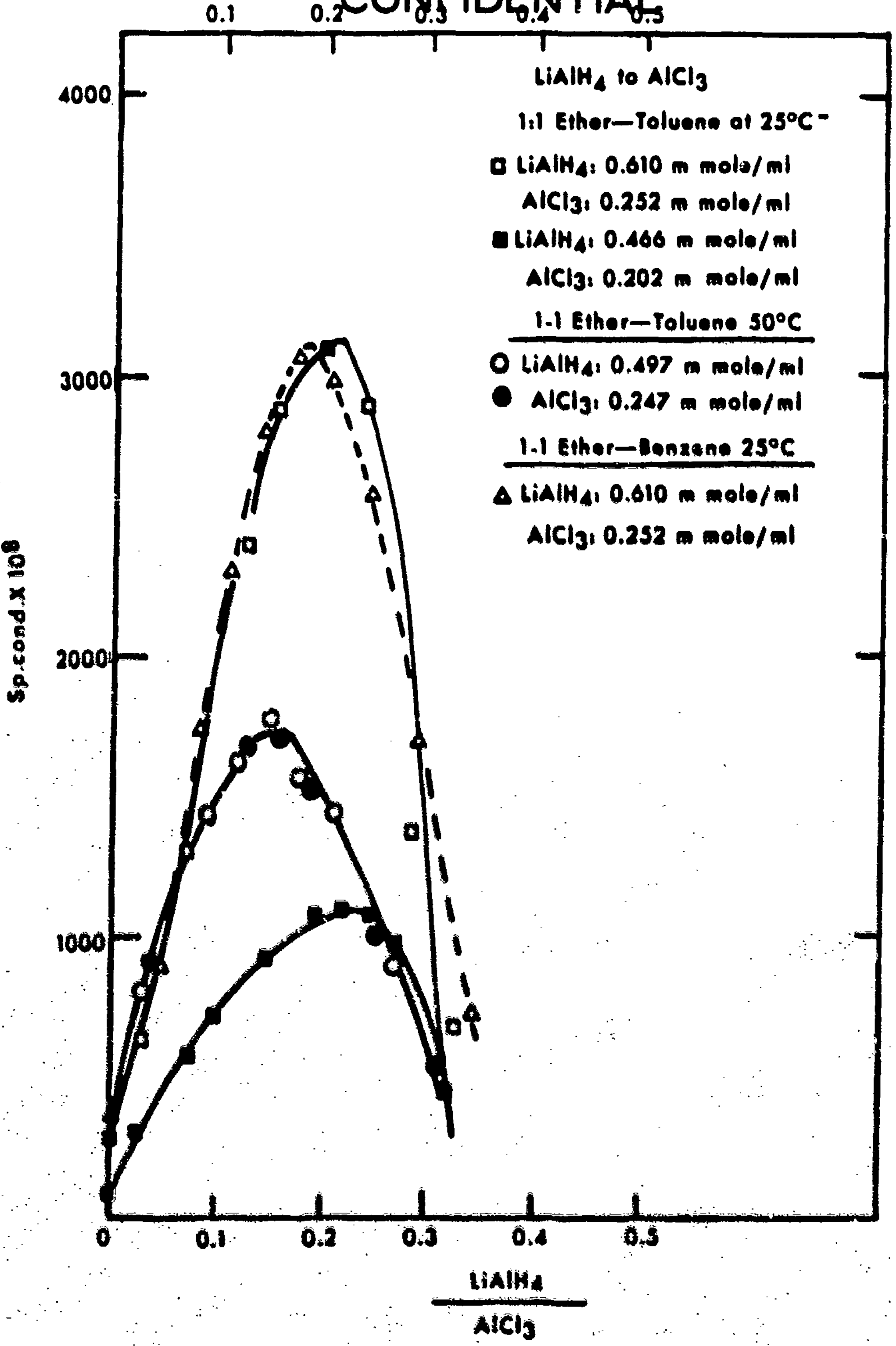


Figure 9
ADDITION OF LiAlH4 TO AlCl3 IN ETHER-TOLUENE AND ETHER-BENZENE MIXTURES

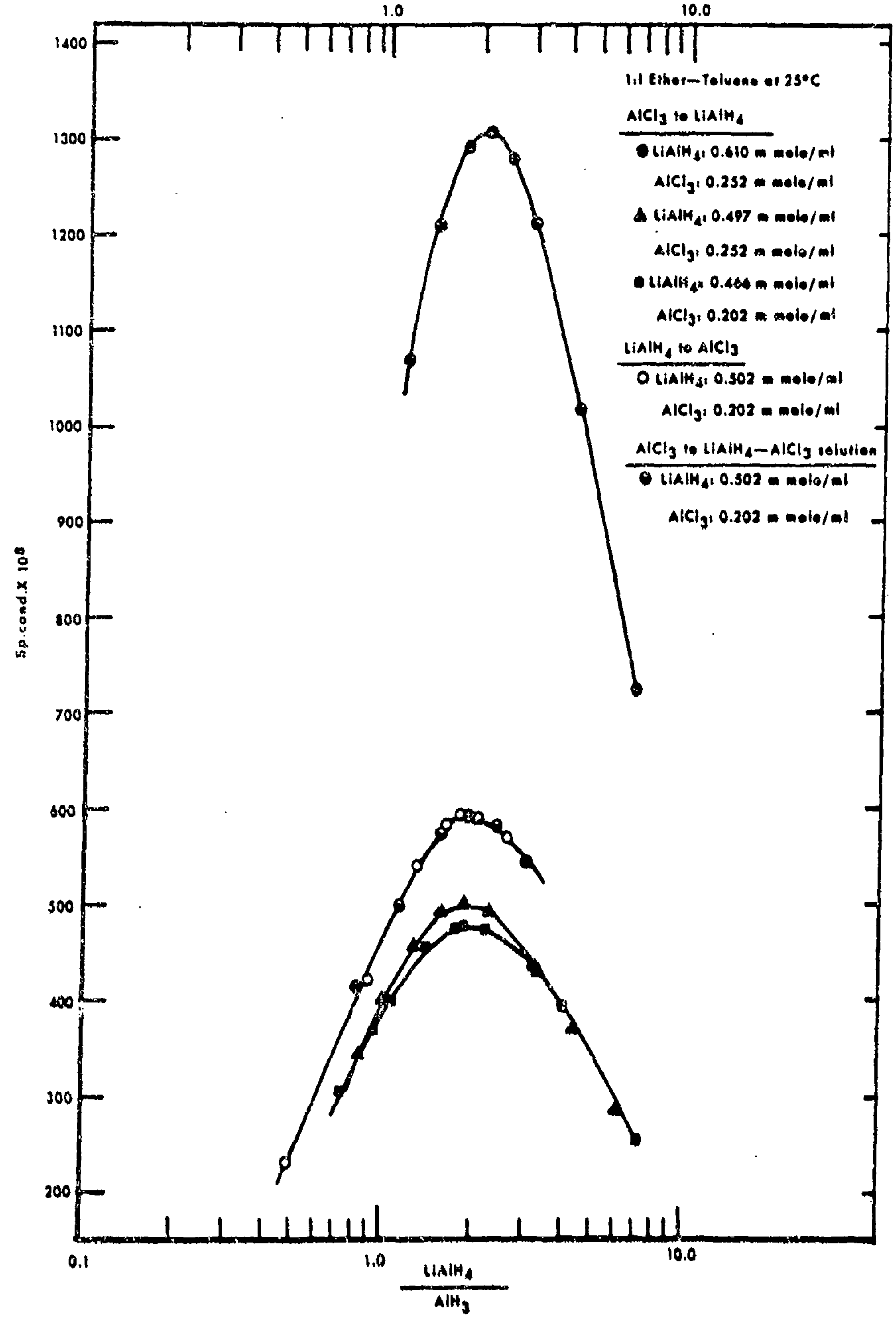


Figure 10
$LiAlH_4$-$AlCl_3$ TITRATIONS IN ETHER-TOLUENE

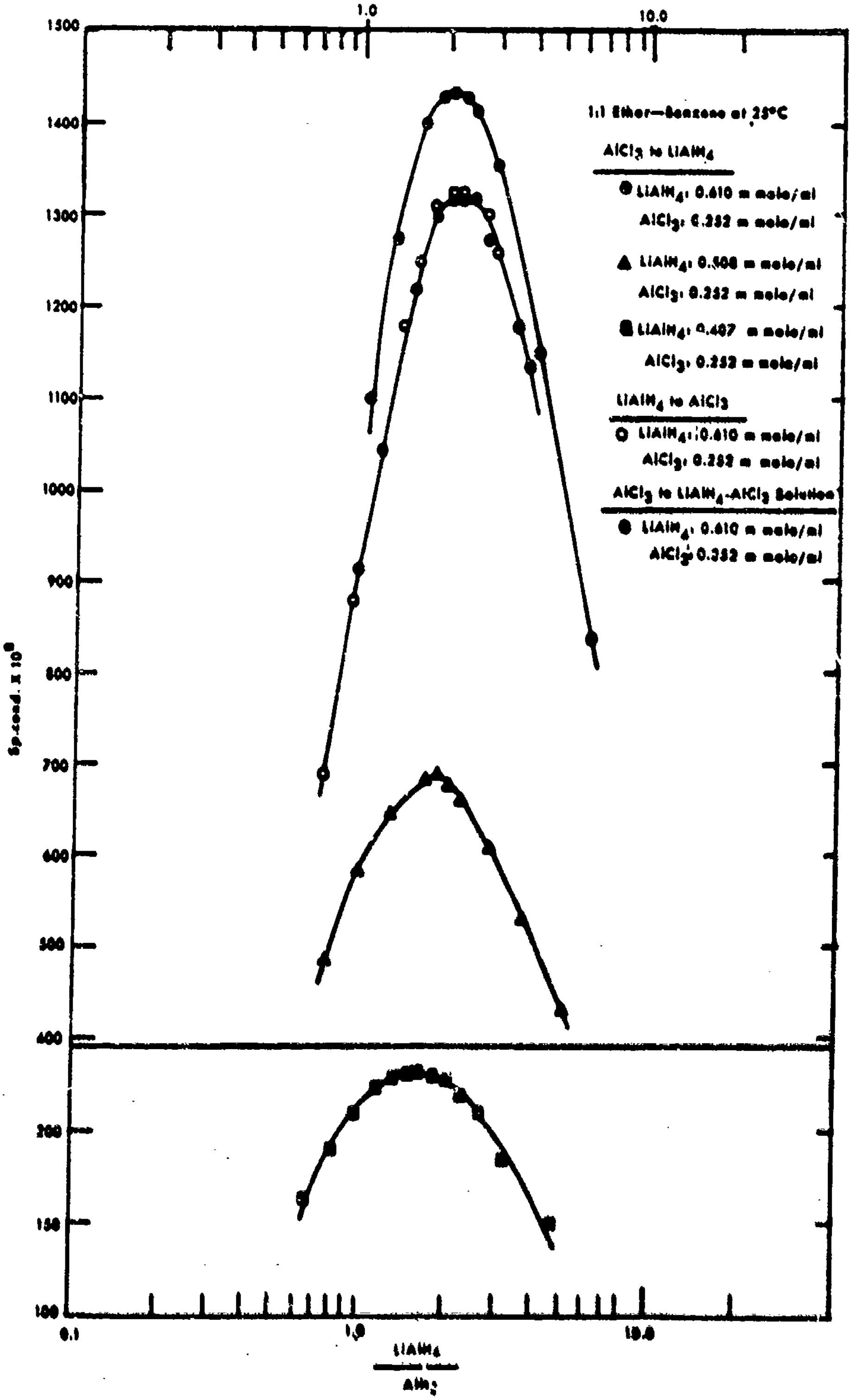


Figure 11

$LiAlH_4$-$AlCl_3$ TITRATIONS IN ETHER-BENZENE precipitate in the cell, no maximum was obtained. Addition of $LiAlH_4$ to filtered equivalent solutions resulted in a conductance maximum at 2.0 for $LiAlH_4/AlH_3$ as in the previous experiments, again the conductivities were less than when LiCl was present. (See Figure 12)

The addition of pure, dry lithium chloride to one of the reactants before the titration was started had no effect on the shapes of the conductivity curves, however, the conductivity values were, in general, higher (5, 6).

An attempt to isolate a complex at the $LiAlH_4/AlH_3=2.0$ failed. When $LiAlH_4$ and $AlCl_3$ are added in the required proportions and the solvents are evaporated at approximately 28-30°C the resulting precipitate is a mixture of Olane 62 and $LiAlH_4$. Although conclusive results have been obtained, the most probable method to obtain the 2:1 complex is to treat the solution as if one were trying to obtain desolvated Olane. That is, heat a ether-toluene or ether-benzene solution of the 2:1 $LiAlH_4$-AlH_3 mixture to approximately 85°C, strip the ether off until the precipitate forms, cool, and filter.

Titrations of $LiAlH_4$ and $AlCl_3$ ether solutions with toluene show, as expected, that there is no ionic interaction of the toluene with either solute.

Figure 13 shows the results of titrations involving $LiAlH_4$ and $LiBH_4$ in pure ether. There apparently is no strong ionic interactions between the two compounds.

In Table XVI are listed data obtained near the maximum conductance where excess $AlCl_3$ is present. Column 1 lists the solvent system. The temperature at which the titrations were carried out is given in column 2. The pairs of values listed in column 3 and 4 bracket the maximum conductance value, i.e., the maximum conductance lies somewhere between these two points.

It is very appealing to believe that the conductance maximums correspond to whole numbers for the $AlCl_3/AlH_3$ ratios. This

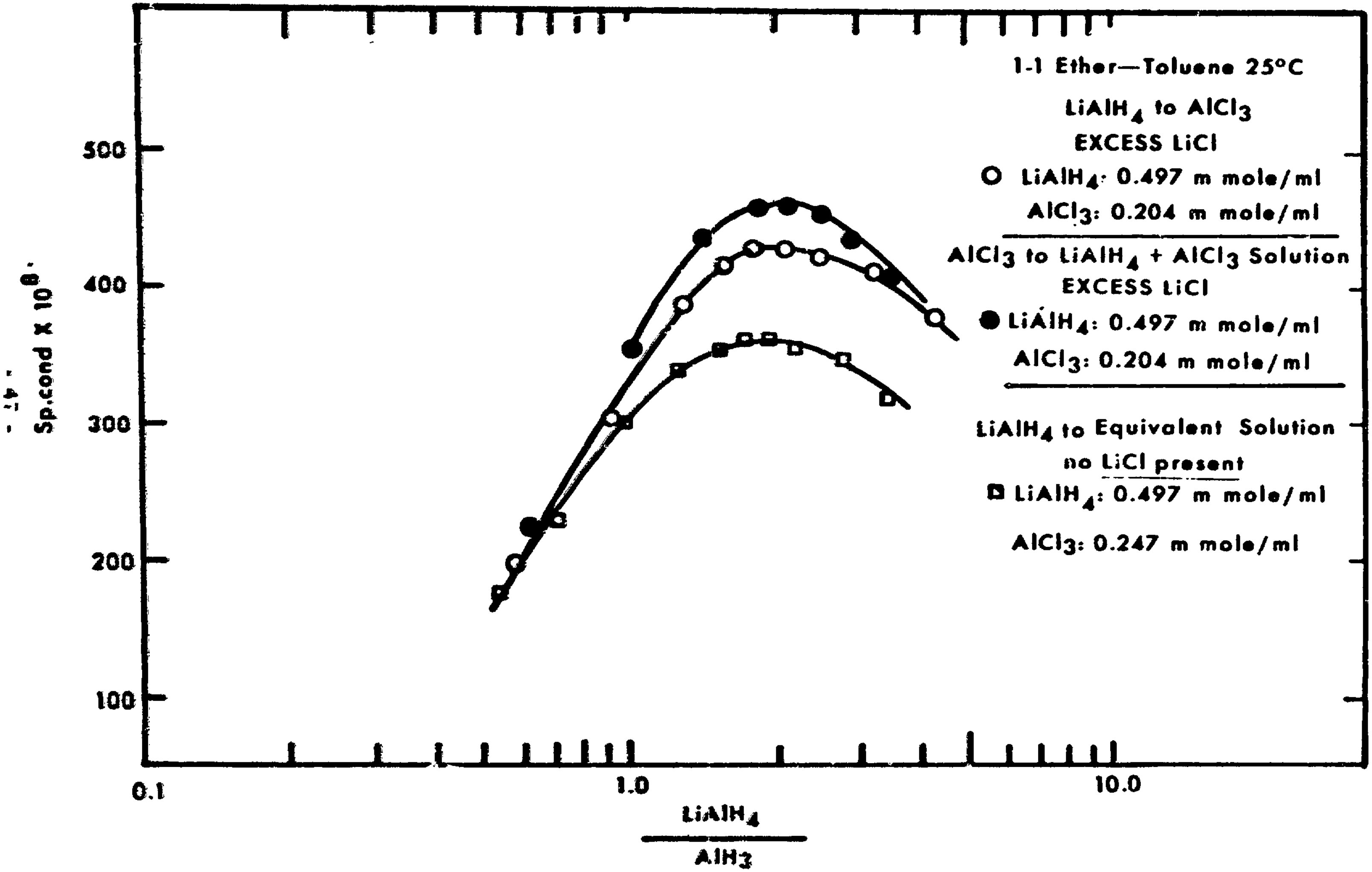


Figure 12
EFFECT OF LiCl ON THE LiAlH -AlCl3 TITRATION

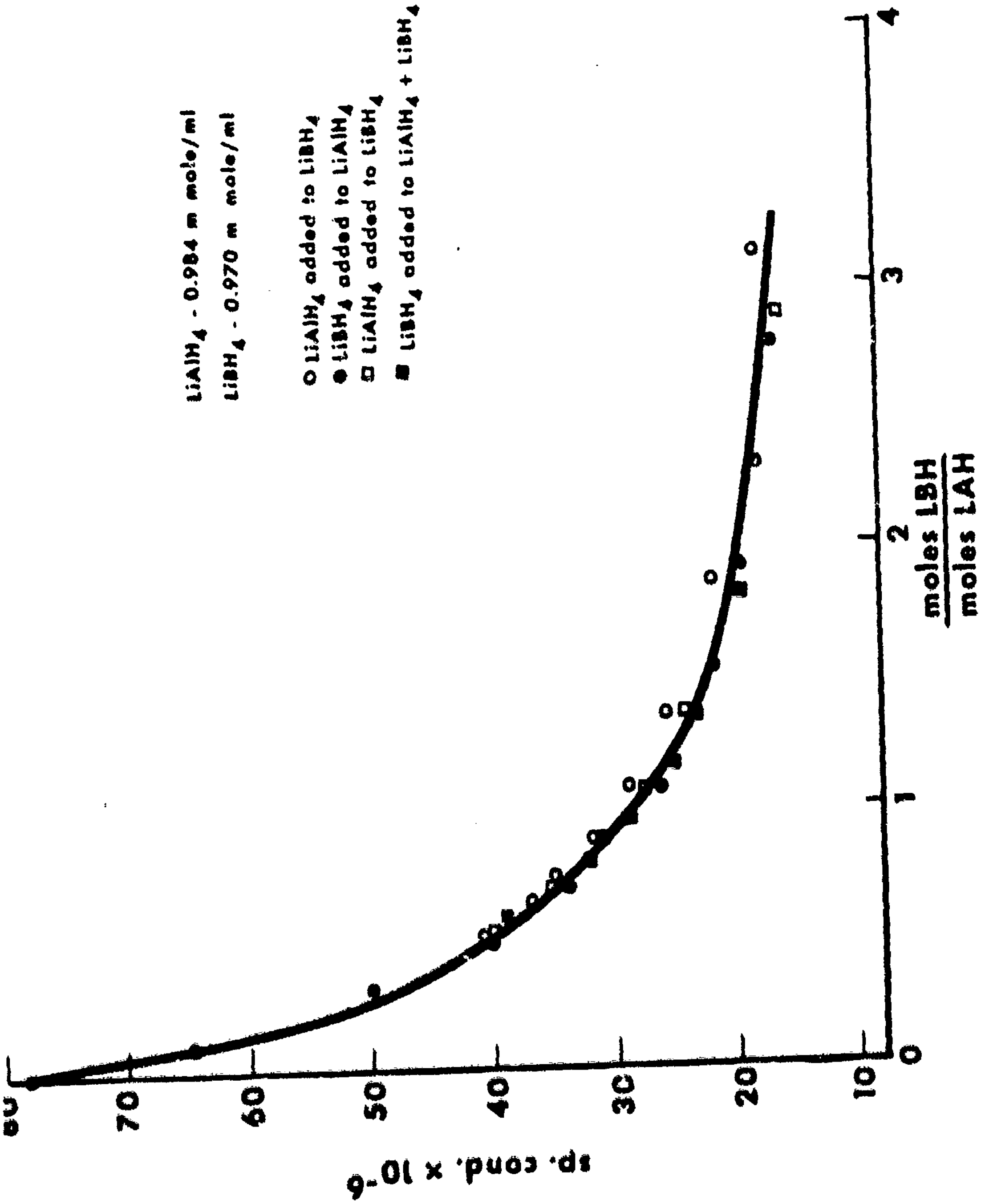


Figure 13

$LiAlH_4$-$LiBH_4$ TITRATION IN ETHER AT 25°C

TABLE XVI

RATIO OF SPECIES IN DIFFERENT SOLVENTS

System	Temp. °C	$\frac{LiAlH_4}{AlCl_3}$	$\frac{AlCl_3}{AlH_3}$
Ether	25°	0,322 - 0,365	2,07 - 1,80
		0,315 - 0,359	2,13 - 1,84
Ether-Toluene	25°	0,201 - 0,252	3,48 - 2,73
		0,219 - 0,244	3,17 - 2,82
	50°	0,151 - 0,180	4,72 - 3,92
		0,161 - 0,211	4,41 - 3,30
		0,158 - 0,188	4,50 - 3,74
Ether-Benzene	25°	0,177 - 0,201	3,99 - 3,48
		0,176 - 0,206	4,01 - 3,40

would indicate that a certain number of moles of $AlCl_3$ interact with each mole of AlH_3, depending on the temperature and solvent system. However, if this were the case the maximum conductance should be reached independent of the mode of mixing the $LiAlH_4$ and $AlCl_3$. This is not the case, because the maximum is only obtained when $LiAlH_4$ is added to the $AlCl_3$ and not vice versa.

On the other hand, the ratio of 2.0 for the $LiAlH_4/AlH_3$ ratio is independent of the way that $LiAlH_4$ and $AlCl_3$ are added to each other. Also the specific conductance value for the maximum was approximately 10 times higher than the original $LiAlH_4$ solution and several hundred times the conductance of AlH_3 ($LiAlH_4/AlCl_3 = 3.0$). This indicates that there is interaction between the $LiAlH_4$ and AlH_3.

5. Solubility Studies

In an effort to obtain single crystals of Olane 58 of larger particles size, a number of solvents were investigated as possible crystallizing media for either Olane 58 or Olane 60. The results of these studies are summarized in Table XVII. The low temperature experiments in ether were an attempt to determine if Olane 58 had a reverse solubility, similar to that of some inorganic compounds. There was not evidence, however, that this was the case. Preliminary results indicate that dimethylformamide solubilizes or complexes with Olane 60 at higher temperatures. X-ray results revealed that all of the Olane 60 was removed from an Olane sample analyzing predominantly Olane 60. The exact nature of this complex in solution could not be determined from infrared analysis due to interference from the carbonyl group in the Al-H absorption region, even with matched cells.

TABLE XVII

SOLUBILITY STUDIES

Olane Form	Solvent	Time	Temp.	Comments
OLANE 58	Ethyl Ether	5 days	0°C	No evidence for solubility or increase in particle size.
		5 days	-78°C	See above comment.
	THF	4 days	r.t.	No evidence for solubility or complexing.
	THF		65°C	Slight solution or complexing based on IR.
	DMSO	18 hours	r.t.	No reaction or solution.
	DMSO	6 hours	90-95°	No reaction or solution.
OLANE 60	DMSO	18 hours	r.t.	No evidence from IR for solution or complex.
	DMSO	6 hours	80-85°	See above comment.
	DMF	72 hours	r.t.	X-ray on residual solids indicate no solution. Infrared indefinite.
	DMF	3 hours	85°	Olane 60 removed from a sample which analyzed only 7 percent Olane 58.

C. Testing and Evaluation

As numerous samples of improved Olane 58 became available under this program the mere logistics of the studies became significant to say nothing of the time involvement, equipment failures, and power shutdowns. As a consequence, Olin sometime ago began investigating faster means of determining a thermal stability of Olane and attempting to relate the results to the 60°C Taliani Test.

1. Taliani Studies at 100°C

In earlier studies (1) Olin compared the 60° and 100°C thermal stability Taliani Test (Table XVIII) using the 60°C/73 hr. and 100°/4 hr. test as comparison. Unfortunately as we now look upon this comparison, a poor choice was made since we are not comparing the same percentage decomposition in the two cases. As has later been determined by Olin and others, in the first stage of the "decomposition" the initial gases consist of, in many cases, diethyl ether, toluene, and their decomposition products which are impurities in the Olane 58. As a result, the "decomposition" measured in the 60°C/72 hrs. can be seriously affected by the thoroughness of washing and drying of the samples. Because of this problem, Olin again investigated the problem comparing the result in the one percent decomposition area in both 100° and 60°C tests. In general, the correlation was found to be good with respect to time order. This enabled continued evaluation at the higher temperature for screening purposes. Comparisons are tabulated below and illustrated in Figure 14.

One Percent Olane Decomposition

60°(days)	100°(hr.)
8	3.5
14	4.5
20	5.25
24	6.25
43	7.5
51	9.5
60-70	12.5

TABLE XVIII

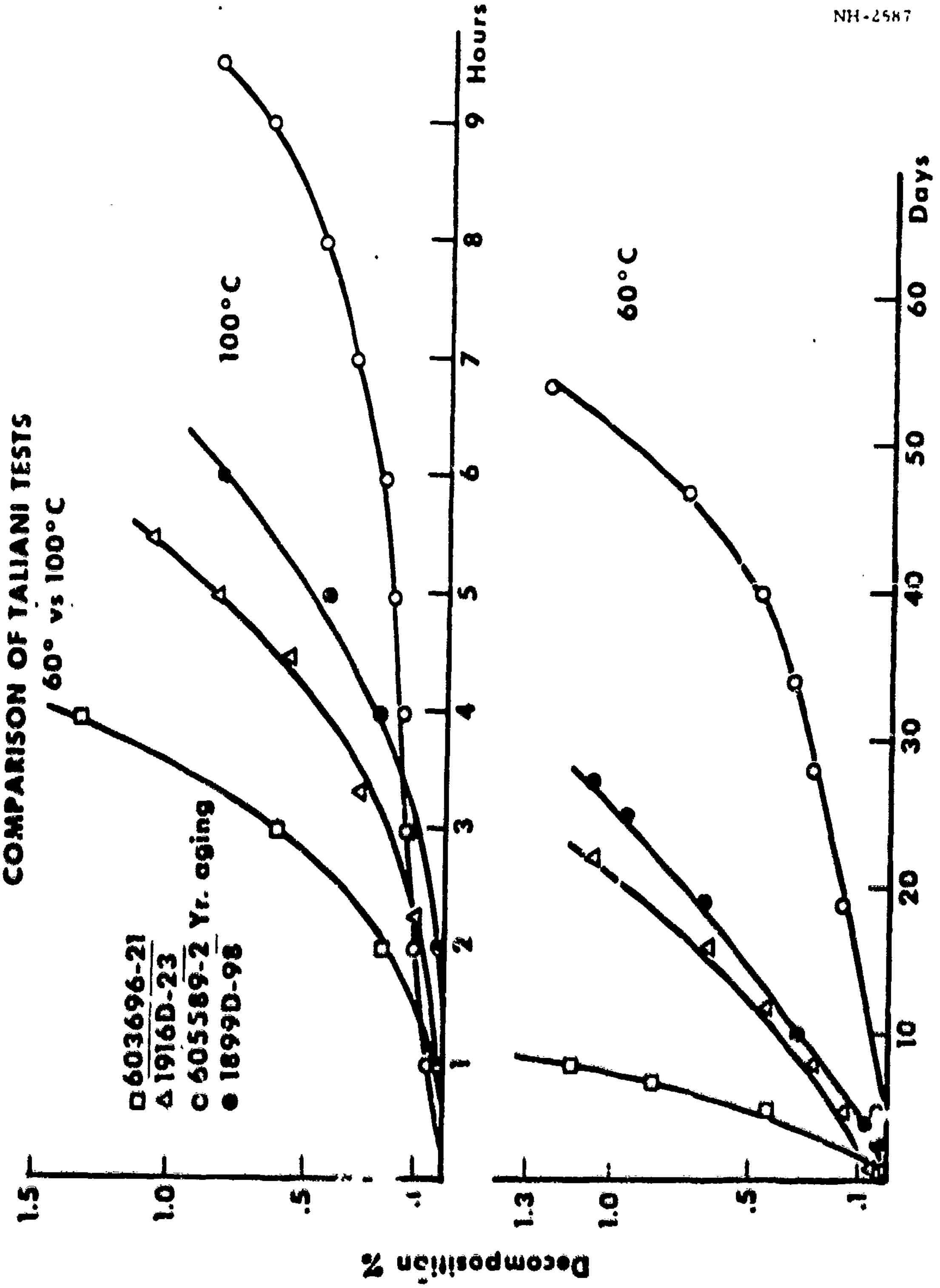
COMPARISON OF THERMAL STABILITY AT 60° AND 100°C

% DECOMPOSITION

Sample	60° for 72 hours	100° for 4 hours
A-D-72	0.20	0.89
C-88-2	0.17	0.19
C-72	0.25	1.35
C-73	0.23	0.69
600822	0.18	0.76
600828	0.10	0.46
600825	0.15	1.61
600849	0.12	0.15
600856	0.75	1.00
600560	0.09	0.26
600873	0.32	0.69
600870	0.07	0.22
600867	0.12	0.43

NH-2587

Figure 4
COMPARISON OF TALIANI TESTS
60° vs 100°C



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As a result initial testing of Olane 58 was performed at 100°C to first determine any improvements made in the thermal stability of the material by the research studies. In those cases where samples of good thermal stability were obtained further testing at 60°C was also conducted.

2. Differential Scanning Calorimetry

One approach which received attention was the use of the Differential Scanning Calorimetry (DSC). The versatility of results have been thoroughly reviewed in previous reports.(1) Initial efforts to correlate thermal stability at 60°C Taliani with DSC results at 150°C were not fruitful.

A re-evaluation of this data from the DSC studies (Differential Scanning Calorimetry) was made in an effort to uncover significant corelations between the Taliani decomposition test and the isothermal decomposition at 150°C. The factors which appear to offer some guide lines were:

1. Induction Time
2. Average Total Decomposition Rates
3. Decomposition in 10% Total Time
4. Average Rate over 10% Total Time

On the basis of these interpretations, a DSC isothermal scan at 150° performed on sample No. 605589 synthesized by the solid $LiAlH_4$ process indicated superior stability. However, no firm correlations are indicated. The results as compared to previous data are provided in Table XIX.

As a result of the lack of correlation a more [illegible]nsive study was undertaken. This investigation was divided into three areas, namely:

a. Normal Programmed Scan
b. Slow Programmed Scan
c. Isothermal Scans at 150°C and at [illegible] °C

Throughout the whole investigation the DSC system was continuously swept with argon.

TABLE XIX

DSC ISOTHERMAL STUDIES 150°C

Sample	Mode of Prep.	Taliani Decomposition 1% - 60°C (days)	Sample Wt. (mg.)	Induction Time (min.)	Total Decomp. (min.)	Average Decomp. Rate (min./mg.)	Decomp. in 10% total time (%)	Decomp. Rate over 10% total time (min./mg.)
Olane 57		2	2.35	0	5.5	2.3		
Chloride-Free Standard		6.3	3.17	3.6	18.6	5.9	2.1	27.8
Standard		7.3	3.03	3.1	12.2	4.0	2.6	14.9
6058-25	MBT	15	2.69	2.5	24.3	9.0	4.5	20
6058-55	PTA	18.3	3.52	3.1	11.0	3.13	1.3	24
6055-63	Simult. addition	20.3	2.33	8.0	14.6	6.3	2.5	25
6058-22	MBT	22	2.89	3.0	17.3	6.0	3.7	16
605570	Solid LAH	22	1.94	3.1	14.8	7.6	1.9	40
605569	Solid LAH	31	2.57	6.3	15.4	6.0	1.8	33.6

a. Normal Programmed Scan

This scan was conducted at a heating rate of 20°C/min. and at a range of from 8 to 32 depending on the sample size. The area under the curve was measured with a planimeter and correlated with the area obtained upon melting a known weight of pure indium. The heat of fusion of indium (99.99% purity) was taken as 6.8 cal./gram. Table XX details the results of these determinations.

b. Slow Programmed Scan

This scan was conducted at a heating rate of 50°C/min., starting at a temperature of 100°C and under high resolution, i.e. a range of 4. It was hoped that both the time of induction and the temperature at which decomposition started could be accurately and reproducibly measured. In some cases one break in the baseline was observed and in other cases, two such breaks were observed. The results are given in Table XXI.

c. Isothermal Studies at 150° and 160°

The weighed sample was placed in the detector head and programmed under normal conditions from 100°C to 150°C. At 150°C the programmer was stopped and the recorder continued to run. The area traced out was very broad extending from 10 to 30 inches of chart paper. The area under the curve was measured with a planimeter.

Since the % weight loss fell within the theoretical limits, it was felt that the factor $\left(\frac{\text{Range Area}}{\text{wt.}}\right)$ could give some indications concerning the thermal stability of the samples. Table XXII gives the results obtained at 150°C and Table XXIII gives the results obtained at 160°C.

Efforts to relate the foregoing results to data obtained from Taliani testing at 60°, 80° and 100° to one percent decomposition were not successful. In the DSC study, sampling techniques and handling procedures

TABLE X

PROGRAMMED 20°C/MIN.

Sample No.	Init. wt. (mg.)	% Loss	Temp. at Maxima(°C)	ΔH(cal/g.)
607236	2.240	8.93	194	202
607240	2.308	9.36	189	209
607240	1.452	9.64	189	213
S-165-D	2.316	9.50	203	213
S-165-D	1.232	10.3	205	212
1899D-12	1.224	9.80	202	190

TABLE XXI

INDUCTION TIME AND TEMP.

5°C/MIN. - START AT 100°C

Sample No.	Particle Size	Induction Temp. (°C)	Induction Time (min.)
607240	As received	141 to 144.5	
607240	(325-400)	150-149	10.0-9.8
607236	As received	144	
607236	(325-400)	152-153	10.4-10.6
S-165-D	As received	150-155-151	
S-165-D	(325-400)	153-156	10.6-11.2
1899D-12	As received	160-162	
1899D-12	(325-400)	162-155-153	12.4-10.6
1916D-11	As received	143-121-159	

TABLE XXII - Isotherm at 150°C

Sample No.	Wt. (mg.)	Particle Size	% Loss	$\left(\frac{\text{Range . Area}}{\text{Init. Wt.}}\right) 10^2$	Total Time	Ignition Temp.	Induction Time
607240	5.956	As received	9.06	7.91	17.7		
607240	5.376	As received	8.30	8.06	12.7		
607240	4.044		9.49	8.01	12.7		
607240	3.620		8.29	8.66	14.3		
607240	7.756	(325-400)	9.23	7.26	18.7		1.8
607240	4.736	(325-400)	10.6	8.14	18.5		1.8
607236	7.052	As received	9.47	8.01	20.4		
607236	4.924	(325-400)	13.4	7.62	24.2		2.[illegible]
607236	3.680	(325-400)	9.2	7.48	21.0		
S-165-D	7.556	As received	7.83	7.20			
S-165-D	5.456	As received	9.45	6.80			
S-165-D	6.512	(325-400)	10.1	3.75	28		1.7
S-155-D	8.828	(325-400)	9.1	3.85	31.2		4.3
S-165-D	8.336	(0-200)	8.5	3.70		151	
S-165-D	8.020	(200-325)	9.1	3.66		154	
S-165-D	7.632	(325-400)	9.2	3.72		153	
S-165-D	5.908	(400- ∞)	Loss	3.24		153	
1899L-12	6.268	As received	9.51	4.95	24.4		
1899D-12	8.852	(325-400)	8.81	3.66	33.0		3.6
1899D-12	3.460	(325-400)	9.59	5.27	43.0		7.7
1899D-12	7.540	(0-200)	8.64	3.52		152	
1899D-12	1.700	(325-400)	9.41	3.58		144	
1916D-11	12.728	As received	9.18	0.74	16.3		

TABLE XXIII - Isotherm 160°C

Sample No.	Wt (mg.)	% Loss	Time (min.)	$\frac{(\text{Range} \cdot \text{Area})\,10^3}{\text{wt.}}$
607236	3.512	9.00	12.3	8.19
607236	5.480	9.34	12.5	8.68
607240	3.276	9.28	10.0	8.10
607240	4.072	9.43	10.0	8.08
607240	6.556	9.39	10.7	8.44
S-165-D	4.292	9.69	17.1	7.94
S-165-D	4.004	14.58	19.7	8.12
S-165-D	4.424	10.22	17.0	8.07
1899D-12	3.992	9.82	17.0	7.48
1899D-12	2.040	10.9	17.3	7.94
1916D-11	4.680	4.196	14.6	0.84
1916D-11	2.736	11.3	18.4	2.62
1916D-11	4.220	11.5	16.0	2.43
1916D-11	6.948	9.8	13.4	1.62

were found to be extremely critical. Although the induction temperatures shown in Table XXIII were in the same general order as the sample stability, the variations were too small to permit unequivocal assessments of thermal stability. Furthermore, deviations within a single sample determination were also noted.

It was hoped that the constant derived from the expression, $\frac{\text{Range x Area x } 10^2}{\text{wt.}}$ might offer some insight into the thermal characteristics of a given sample. The assumption was based on the fact that the more stable samples would evolve heat at a much slower rate. Some of this dissipated heat would not be measurable by the detector unit and thus cause the measured area under the curve to be correspondingly smaller. Although there are some indications from the data in Tables XXII and XXIII that this may be true the magnitude of the differences and deviations from one sample to another did not permit ready comparison to Taliani data.

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APPENDIX A - Synthesis

I. Apparatus

A one-necked one-liter or a three-liter flask was used for the synthesis. The conversion apparatus consisted of a three-liter, three necked, round-bottom flask, equipped with a thermometer, a "Lew" stirrer, a still head with a water-cooled condenser, and a dry-ice acetone cooled one-liter receiver.

II. Reagents

A. $AlCl_3$, (anhydrous reagent ACS) Baker and Adamson, Code 1230.

B. $LiAlH_4$, (95+ percent pure) Metal Hydrides, Inc.

C. Ether, distilled from $LiAlH_4$ prior to use.

D. Toluene, (reagent ACS) Baker and Adamson, Code 2398.

E. $LiBH_4$, Metal Hydrides, Inc.

F. $LiAlH_4$, (99.4% pure) Prepared by recrystallization from toluene ether solution.

G. Phenothiazine, Fisher Scientific Company.

III. Procedure

Method A - Solid Addition

1. Toluene-Ether 2:1 (Experiment No. 606639)

To the reaction flask was added 0.125 moles of $AlCl_3$ in 900 mls. of ether. While stirring, 0.463 moles of solid crude $LiAlH_4$ was added in small increments. This process took approximately 15 minutes; after which 0.090 moles of $LiBH_4$ in 100 mls. of ether was added. The stirring was continued for 30 more minutes and 2000 mls. of toluene was added. This mixture was filtered into the three-liter flask and processed as follows.

Time	Bath Temp. °C	Pot Temp. °C	Pressure	Remarks
1	60	45	390	
10	60	47	350	
25	62	47	250	
40	62	50	240	
65	62	49	120 Olane 62 p. p. t.	2.5% Et_2O
95	104	90	740	
100	104	95	Atmos.	
102	104	100	Atmos.	
125	104	100	Atmos.	

The final product after washing with ether was Olane 58 as indicated by X-ray analysis.

2. Toluene-Ether 3:1 (Experiment No. 606645)

To 667 mls. of ether containing .0439 moles of $AlCl_3$ was added .1677 moles of crude solid $LiAlH_4$, while stirring with a magnetic stirring bar. After 30 minutes .0319 moles of $LiBH_4$ was added in 33 mls. of ether. The stirring was continued for 15 minutes more after which 2100 mls. of dry toluene was added. This solution was filtered into the desolvation flask and processed as follows:

Desolvation 606645 3:1 Process

Time	Bath Temp. °C	Pot Temp. °C	Pressure	Remarks
1	65	45	310	
10	65	50	220	
30	68	50	160	7-8% Et_2O
31	70	52	460	
44	92	75	510	
54	102	90	610	
50	104	95	660	
69	104	97	670	
62	104	97	720	
64	104	98	730	particles formed
79	104	98	Atmos.	

The product was Olane 58.

Method B - Direct Crystallizations

1. Conversion at 75°C (Experiment No. 603696)

All equipment was oven-dried and taken into the dry box prior to use. The stock solutions of reagents ($AlCl_3$, $LiAlH_4$, $LiBH_4$) used were approximately 1 molar in ether. To the 3-liter flask were added 0.025 moles of $AlCl_3$ diluted with make-up ether, 0.091 moles of $LiAlH_4$ and 0.18 moles of $LiBH_4$ successively.

This solution was then diluted with 2400 ml. of toluene (dried with ethereal ($LiAlH_4$). The total ether content of the mixture was 400 ml. The precipitated LiCl was allowed to settle after which it was filtered into the conversion flask through the fritted-glass filter.

The ether was stripped off under reduced pressure at approximately 40° until the content was 5 percent by weight in the solution. The conversion system was brought to ambient pressure with nitrogen and then heated as rapidly as possible to 75°C, where it was held for five hours. Solids formation occurred during the holding period at 75°C. The precipitation time was found to vary somewhat from one experiment to another. The reasons for this are not obvious at present. The heating was then terminated, and the product was isolated by the usual procedures. The desolvation and conversion conditions follow.

Time (min.)	Bath Temp. °C	Pot Temp. °C	Pressure (mm. Hg)	Remarks
0	60	40	185	
5	60	40	170	
10	60	40	130	
15	60	40	92	
25	68.5	53	Atmospheric	
35	79	70	"	
40	79	75	"	
75	79	76	"	Crystals (few)
225	79	76	"	Crystals (many)
340	79	76	"	

The slurry was cooled and filtered. The solid were washed with ether and dried under vacuum. An X-ray analysis indicated the product to be 100°/, Olane 58.

2. Conversion at 95°C (Experiment No. 607489)

All equipment was oven-dried and purged with nitrogen prior to use. The stock solutions of reagents ($AlCl_3$, $LiAlH_4$, $LiBH_4$) used were approximately 1 molar in ether. To the 1-liter flask was added 0.023 moles of $AlCl_3$.

This solution was then diluted with ether prior to the addition of 2100 ml. of toluene (dried with ethereal $LiAlH_4$). The $LiAlH_4$ (0.10 moles) (35 mole percent excess) was next added with magnetic stirring of the solution. The stirring was continued for 30 minutes before the $LiBH_4$ solution (0.32 moles) was added with an additional five minutes of stirring. The total ether content of the mixture was 350 ml. The solution was allowed to settle for thirty minutes and then was filtered into the conversion flask through the fritted glass filter.

The ether was stripped off under reduced pressure at approximately 40° until the content was 5 percent by weight in the solution. The conversion system was then pressured to atmospheric with N_2 and heated as rapidly as possible to 80°C where it was held for forty-five minutes. Solids formation occurred during the holding period at 80°. The precipitation time was found to vary somewhat from one experiment to another. The reasons for this are not obvious at present. After the holding period at 80°C, the solution was heated to 95°C as rapidly as possible and held for twenty minutes. During this period the required concentration of inhibitor was added. The heating was then terminated and the product was isolated by the usual procedures. The desolvation and conversion conditions are presented in Figure 1 (see Text page 4). Photos 1 - 4 show the initial precipitate (mixture of Olanes 60 and 58) and its transformation to the final granular form (Olane 58) at 95°C in a typical high dilution process (see Text page 3).

It is possible that a small portion of final product could have resulted via solution phenomena on the basis of current information. The present studies with lower concentrations of aluminum hydride (0.25 - 0.30 molar) and higher dilutions (6:1) have consistently produced a glassy macrocrystalline product of improved bulk density.

Method C - Toluene-Ether 3:1 Process (Expt. No. 606645).

All equipment was oven dried and taken into the dry box prior to use. The stock solutions of reagents ($AlCl_3$, $LiBH_4$ and $LiAlH_4$) used were approximately 1 molar in ether. To the three liter reaction flask was added 0.0439 moles of $AlCl_3$ in 43 mls. of ether and 624 mls. of make-up ether to assure the proper concentration of AlH_3 (.25 mole). The solid $LiAlH_4$ (0.1677 moles) was then added. After the slurry stirred for 45 minutes, the $LiBH_4$ solution (0.0319 moles/33 ml.) was added. The stirring was then continued for 10 minutes after which the toluene (2100 mls.) was added. This mixture was then filtered into the reaction flask.

The ether was distilled under vacuum until 7 - 8% ether remained. The reaction was then brought to 468 mm. Hg and the temperature raised to 100°C. Conditions for a typical conversion follow.

Time (min.)	Bath Temp. °C	Pot Temp. °C	Pressure (mm.Hg.)	Remarks
0	65	45	318	
10	65	50	228	
20	68	50	168	% Et_2O 7 - 8%
Started up to 100°C. Bled in nitrogen to increase pressure.				
21	70	52	468	
25	92	75	518	
35	102	90	618	
50	104	95	668	
65	104	97.5	738	First crystals formed.
88	104	99.5	768(atm.)	

The slurry was cooled and filtered. The solids were washed with dry ether and placed under vacuum for drying. An X-ray analysis indicated the product to be 100% Olane 58.

Method D - Toluene-Benzene-Ether Process (Expt. No. 606674)

To the reaction vessel was added 0.1928 moles of $LiAlH_4$ in 611 mls. of ether. While stirring, 0.0438 moles of $AlCl_3$ in 29 mls. of ether was added. After 45 minutes of stirring, .0658 moles of $LiBH_4$ in 60 mls. of ether and 2100 mls. of 1:1 benzene, toluene were added. This mixture was then filtered and desolvated as follows.

Time	Bath Temp. °C	Pot Temp. °C	Pressure	Remarks
0	70	43	460 m.m.	
15	71	54	490 m.m.	
35	90	63	580 m.m.	
50	90	71	620 m.m.	
75	90	80	730 m.m.	
Paricles growing on flask sides.				
85	90	85	730 m.m.	Particles growing slowly. Placed on total reflux.
160	90	85	730 m.m.	Started to cool both.

The product was all Olane 58 as indicated by X-ray analysis.

Method E - Aluminum Borohydride Process (Expt. No. 606681)

To the reaction flask were added .0468 moles of $AlCl_3$ diluted with 534 moles of make-up ether and .1308 moles of $LiAlH_4$ in 129 mls. of ether while stirring. After 20 minutes .0411 moles of $LiBH_4$ in 38 mls.

of ether was added. The stirring was continued for 20 minutes more after which the 50:50 benzene, toluene (2100 mls.) was added. The reaction was then filtered and disolvated as follows.

Time	Bath Temp. °C	Pot Temp. °C	Pressure	Remarks
0	81	44	430	
15	82	49	500	
35	90	68	580	
45	90	75	620	
60	90	80	650	Put on total reflux.
90	90	80	650	Began to add .0304 moles of LAH in a mixture of 30 mls. ether and 90 mls. Ø, Ø$\mathrm{CH_3}$(50:50).
100	90	78	680	Solution distilling. Approximately 50 mls. of LAH added.
110	90	79	690	LAH addition complete.
150	94	84	730	Particles forming.
180	94	84	730	Heating stopped.

The product was large spheres of Olane 58.

APPENDIX B - Conductometric Studies - Experimental

I. Reagents

A. Aluminum chloride (anhydrous reagent grade, Baker and Adamson) was used without further purification. In several experiments the aluminum chloride was sublimed once prior to use. The general appearance of the conductivity curves using either material was identical (i. e., the maxima and minima occured at the same mole ratios) except for slightly different conductance values. Stock solutions were prepared by adding aluminum chloride in a nitrogen atmosphere to ether cooled in a dry ice-acetone bath. The stock solution was analyzed for chloride by the Volhard method.

B. Lithium aluminum hydride (95+ % pure, Metal Hydrides, Inc.) was recrystallized from ether-toluene prior to use. Product assay by hydrogen evolution indicated better than 99.4% purity. The hydride was redissolved in ether and stored under dry nitrogen. Other stock solutions were prepared by dissolving the crude hydride in ether, filtering and storing under dry nitrogen. All the above procedures were conducted in a dry box flushed with dry nitrogen. Very little difference was noted in the conductivity curves when either solution was used. The stock solutions were analyzed by reacting the hydride with a standard benzene solution of iodine and then back titrating with sodium thiosulfate.

C. Lithium borohydride (Methal Hydrides, Inc.) was further purified and analyzed in the same manner as lithium aluminum hydride.

D. Diethyl ether (anhydrous, Mallinckrodt Chemical Works) was distilled over $LiAlH_4$ prior to use.

E. Toluene (reagent grade, Baker and Adamson) was dried with an ether solution of $LiAlH_4$. The amounts of ether and $LiAlH_4$ (which in most cases were insignificant) were taken into account when ether-toluene stock solutions were prepared.

F. Benzene (reagent grade, Baker and Adamson) was handled similar to toluene.

All solutions were made up by volume. Stock solutions were periodically analyzed to check changes in concentrations, if any.

II. Apparatus

Figure A illustrates the conductivity cell and electrodes. The electrodes are held to the 34/45 inner joint by Viton o-rings which assured an air tight seal. A Teflon sleeve can be fitted over the 34/45 inner joint to maintain an air tight seal. The addition burettes, having a capacity of 100 ml. or 12 ml., depending on the nature of the experiment, are clamped to the cell body. Initially, the entire cell was repeatedly evacuated (through an arm not shown in the diagram) and flushed with dry nitrogen before the addition burettes were filled. However, it was found that if the entire cell assembly (except the cell electrodes) was heated to 140°-150°C overnight, assembled and flushed with dry nitrogen until it cooled to room temperature, the cell was sufficiently dry to be used without hydrolyzing any $LiAlH_4$. The Teflon stopcocks, needle valves and o-rings were kept in a dessicator until the cell was assembled. No stopcock grease was used on any part of the cell assembly.

Conductances were measured by pairs of dipping electrodes having cell constant of 0.100 and 0.0100 cm^{-1}. All conductivities were measured at 1000 cycles with an Industrial Instruments Conductivity bridge, Model RC 16B2. It was necessary to use a fixed resistor in parallel with the electrodes for measurements of conductivities below 1×10^{-3} ohm^{-1} cm^{-1}. Solutions were stirred by a glass enclosed magnet rotated by a magnetic

[redacted]

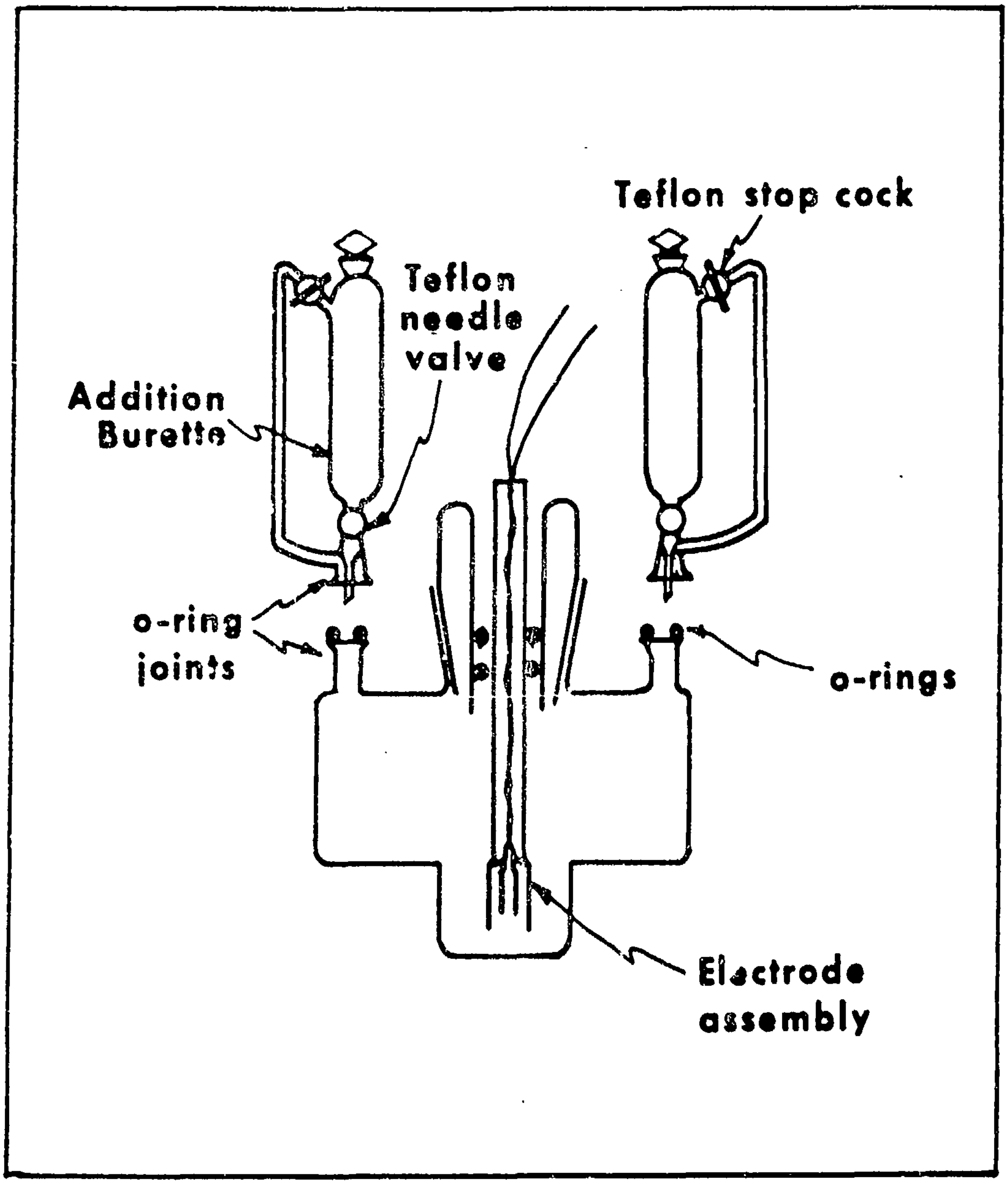

Figure A

CONDUCTIVITY CELL ASSEMBLY

[redacted]

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stirrer. Temperature was controlled at 24.5 ± 0.5°C in air and at 50.0 ± 0.1°C in an oil bath.

III. Procedure

Initially, ether solutions were diluted with equal volumes of toluene or benzene and transfered to the addition burettes in a dry box flushed with dry nitrogen. Later, it was found that the solutions could be transfered into a constant low humidity room without any noticeable difference in the resulting conductivity curves.

One burette was filled with the $LiAlH_4$ solution and the other with the $AlCl_3$ solution. Enough solution from one burette or a mixture from both was added to the cell so that the electrodes were totally immersed. The first conductivity measurement was taken at this point. Subsequent conductivity measurements were taken after each addition of a reactant from one of the burettes. Additions from the 100 ml. burette were read to the nearest millimeter and estimated to the nearest 0.1 ml.; additions from the 12 ml. burette were read to the nearest 0.1 ml. and estimated to the nearest 0.01 ml.

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13 ABSTRACT

(C) The thermal stability of aluminum hydride (Olane 58) has been significantly improved by aging and water treatment. The effect is believed to be due to a surface coating of bayerite, $Al(OH)_3$. These treated samples demonstrated thermal stabilities of less than one per cent decomposition in the Taliani Test at 100°C for 8-12 hours or at 60°C for 50-75 days.

(C) Studies of the synthesis of Olane 58 by the solid $LiAlH_4$ preparatory technique or through the addition of free radical inhibitors did not indicate the superiority of these modifications in present processes.

(C) Direct crystallization of unsolvated aluminum hydride was deomonstrated from a mixed toluene-ether solution.

(C) Although the data from the Differential Scanning Calorimetry (DSC) scans both programmed and isothermal provide some insight into the thermal character of aluminum hydride, no meaningful correlations to Taliani Tests at 60°C and 100°C could be made for decomposition as low as one per cent.

(C) Conductivity studies of the $LiAlH_4$-$AlCl_3$ reaction under a variety of conditions indicate the formation of a $AlH_3 \cdot 2LiAlH_4$ complex and chlorolane species.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
LMH-1						
Olane 58						
Thermal Stability of Olane						

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