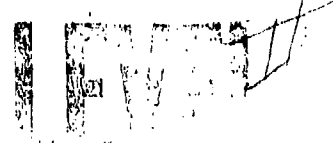


AFWAL-TR-80-4073



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# HIGH SOLIDS COATING SYSTEM

**DESOTA, INCORPORATED**  
RESEARCH AND DEVELOPMENT CENTER  
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JUNE 1980

TECHNICAL REPORT AFWAL-TR-80-4073  
Final Report for period February 1979 to February 1980

Approved for public release; distribution unlimited.

MATERIALS LABORATORY  
AIR FORCE WRIGHT AERONAUTICAL LABORATORY  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45488

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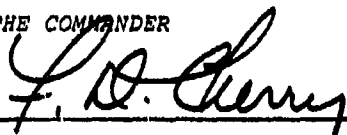
This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



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cont.  
20. One formulation, consisting of a combination of Acryloid AU-568 (oxazolidine), NIAX PCP-0300 (polyol), and Desmodur N-100 (polyisocyanate) was developed under the initial contract and found to exhibit performance properties closely approximating the program goals. During the present contract, this formulation was further evaluated. Attempts to upgrade the properties not meeting the performance specifications were made.

Also, new commercially available resins were evaluated for incorporation into the high solids systems.



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PREFACE

This report covers the period from February 5, 1979 to February 29, 1980 under contract number F33615-79-C-5007 for the Materials Laboratory, Air Force Systems Command, Aeronautical Systems Division, Wright-Patterson AFB, Ohio. The contract entitled "High Solids Coating Systems", was initiated under Project number 2422, "Protective Coatings and Materials", Task number 2422-01, Coatings for Aircraft and Spacecraft. The objective was to develop a 65% volume solids topcoat formulation which, under ambient conditions, would form high performance films suitable for application by airless electrostatic spray.

The project engineers designated were Mr. Daniel E. Prince from February 1979 to July 2, 1979, and Mr. Robert A. Winn from July 2, 1979 through February 29, 1980. This report, which concludes the contract, was released by the authors on April 1, 1980.

Appreciation is extended to the numerous resin suppliers for cooperation in providing samples for evaluation.

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TABLE OF CONTENTS

I. Introduction	1
A. Historical Background	1
B. Description of Chemistry	2
C. Summary of Initial Contract	5
II. Results and Discussion	8
A. Continued Evaluation of Formulation 2408-9	8
1. Long-Term Stability of the Polyol Component	8
a. At Ambient Temperatures	8
b. At Elevated Temperatures	11
2. Pot-Life Study	16
a. Catalyst Variation Study	16
b. Effect of Additives	18
c. Comparison of Raw Materials	27
d. Effect of Volume Solids on Pot-Life	28
3. Flexibility Properties	30
4. Foaming and Sagging	30
5. Correlation between Coating Formulations and Properties	32
6. Reactive Diluents	36
B. Cargill 5770 Evaluation	36
1. Initial Evaluation	36
2. Blending Study	38
3. Continued Evaluation of Formulation 2408-171	40
C. Evaluation of DeSoto Polyester Resin	43

TABLE OF CONTENTS  
(continued)

	<u>Page</u>
III. Conclusions	50
IV. References	52

LIST OF ILLUSTRATIONS

<u>FIGURE</u>		<u>PAGE</u>
1	Effect of TEA Addition on Viscosity of Polyol-Oxazolidine Mixture	9
2	Effect of TEA Addition on Viscosity of Polyol-Oxazolidine Pigmented Mixtures	12
3	Effect of Accelerated Aging on Pot-life of Acryloid AU-568/NIAX PCP-0300/TiO <sub>2</sub> Pigment Grind	14
4	Effect of Accelerated Aging on Pot-life of Acryloid AU-568/TiO <sub>2</sub> Grind Mixed with Desmodur N-100	17
5	Formulation 2408-9 Catalyst Variation Study	19
6	Effect of Tetraethylorthosilicate (TEOS) on Pot-life of Acryloid AU-568/NIAX PCP-0300 System Mixed with Desmodur N-100	20
7	Effect of Additives on Pot-life of AU-568/NIAX PCP-0300 Grind (immediately after preparation)	23
8	Effect of Additives on Pot-life of AU-568/NIAX PCP-0300 Grind (stored 68 days at 77°F)	24
9	Effect of Additives on Pot-life of AU-568/NIAX PCP-0300 Grind (stored 68 days at 100°F)	25
10	Effect of TEOS on Pot-life After Storage	26
11	Pot-life of Formulation 2408-9 at Varying Volume Solids	29
12	Pot-life (time) vs. Volume Solids of Formulation 2408-9	31
13	Effect of Accelerated Aging on Pot-life of Acryloid AU-568/Cargill 5770/TiO <sub>2</sub> Grinds Mixed with Desmodur L-2291	44
14	Pot-life vs. Percent Volume Solids (2651A-93 Polyester Resin)	47
15	Determination of Optimum Volume Solids with Respect to Pot-life	48



LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1	Comparison of Typical Performance Specifications	3
2	Formulation 2408-9 Composition	6
3	Performance Properties of Formulation 2408-9	7
4	Effect of High Temperature Aging on the Viscosity of Pigment Grinds	13
5	Effect of Accelerating Aging of Pigment Grind on Coating Properties	15
6	Effect of Accelerated Aging on the Viscosity of a Pigment Grind (Acryloid AU-568/TiO <sub>2</sub> )	16
7	Effect of Additives on Long Term Stability Grind Compositions	22
8	Analysis of Raw Materials	28
9	Data on Independent Variables and Interaction as used in Regression Analysis	34
10	Response Data used in Regression Analysis	35
11	Correlation of Properties and Compositions	37
12	Formulation 2408-171 Composition	40
13	Performance Properties of Formulation 2408-171	41

## SUMMARY

As part of a continuing effort towards the development of a 65 percent volume solids, polyurethanes exterior aircraft topcoat, one formulation previously developed was extensively evaluated for its ability to meet the full range of performance specifications. The formulation was a pigmented blend of Acryloid AU-568 (oxazolidine), NIAX PCP-0300 (polyol), and Desmodur N-100 (polyisocyanate).

An alternative approach toward this end result was to evaluate new commercially available resins. A formulation consisting of a blend of Acryloid Au-568, Cargill 5770 (polyol), and L-2291 (isocyanate) was developed and exhibited properties close to the program requirements.

Evaluation of these formulations indicated that the difficulties in meeting the performance specifications were in the areas of viscosity, stability, and flexibility of the formed films. The problems, upon further study were found to be inherent to the oxazolidine material.

## I. Introduction

### A. Historical Background

In recent years, the effect of the varied industrial effluents and waste materials which find their way into the environment has come under scrutiny. For the coatings industry and coatings users, the main concern is the solvent emission from the application of paints. Historically, the first environmental constraints were applied to the type of solvents emitted into the atmosphere in an effort to reduce the photochemical smog production (Rule 66, Los Angeles County). These regulations were designed to control the amount of photochemically reactive solvents in relationship to the other, acceptable solvents. The total amount of solvent emission was not controlled. More recently, however, economic parameters, coupled with the energy crisis and an increased awareness of impacts on the environment, have lead to pressures to reduce the total amount of solvent emission. The main choices available to the coatings industry are water-based systems, ultraviolet light curable systems, and/or high solids systems. One of the more attractive approaches for the aerospace industry is high solids coating systems.

High solids coating systems offer a number of attractive properties regarding both economic and environmental concerns. This type of coating can eliminate the use of photochemically reactive solvents as well as drastically reduce the total solvent emissions necessary to deliver equivalent quantities of paint products. This reduction in total solvent and in-

Increased paint solids can result in economic gains through decreased freight, handling, and storage costs. Production rates can be increased, and fire hazards can be reduced. The materials used in high solids systems should be similar to currently used materials so that only minor changes in production and application equipment can be expected.

Various approaches to the development of a high solids high performance exterior aircraft coating were investigated under contract F33615-77-C-5101. One of the most promising coatings studied under this contract was an oxazolidine prepolymer blended with polyisocyanates. A major deficiency with this and other systems was the balancing of flexibility properties while maintaining hardness and chemical resistance. This program, supported by the Materials Laboratory, Wright-Patterson Air Force Base under contract F33615-79-C-5007, is part of a continuing effort begun under contract F33615-88-C-5101.

The performance specifications, Mil-C-83286B "Aliphatic Isocyanate Urethane Coating for Aerospace Application" established by the Air Force, are more stringent than those followed by other coating users. A comparison of the high performance properties required for military aircraft to those of Fruehauf Engineering may be found in Table 1. The performance specifications for Fruehauf Engineering, a truck manufacturer, are considered to be representative of the transportation industry.

#### B. Description of Chemistry

The theory behind polyurethane chemistry is not complex. Hydroxy terminated prepolymers (polyols) are reacted with isocy-

TABLE 1

Comparison of Typical Performance Specifications

MIL-C-83286B	FRUEHAUF ENGINEERING
5% Salt Spray	No blistering, cracking, corrosion, or loss of adhesion after 500 hours of exposure.
100% Relative Humidity	No blistering, cracking, softening, or loss of adhesion after 720 hours of exposure.
Accelerated Weathering	After 500 hour exposure the coating should exhibit 60% impact flexibility, no more than 10% loss of original gloss, and no color change.
Film Resistance	A decrease of no more than one pencil hardness unit after immersion in water (4 days, 100°F), lubricating oil (24 hours, 250°F), hydrocarbon fluid (7 days, room temperature), and hydraulic fluid (7 days, room temperature). A decrease of no more than two pencil hardness units after immersion in Skydrol 500B fluid (7 days, room temperature).
Film Flexibility	No cracking, crazing, or loss of adhesion of coating when elongated 60% by impacting mandrel.
Low Temperature Flexibility	No cracking or loss of adhesion when bent around 2/8 in (9.5mm) diameter cylindrical mandrel after four hours at -55°F (-54°C). (Test immediately after removal from cold box).
High Temperature Resistance	No loss of adhesion or flexibility after four hours at 149°C. (300°F)
Reverse Impact	Not applicable.
600 Gloss	>90
	>80 in-lbs.
	>90
	Not applicable.
	Not applicable.
	No blistering, cracking, corrosion or loss of adhesion after 500 hrs of exposure.
	Not applicable
	No color change, chalking, checking, or other film defects after 250 hours of exposure.
	No cracking, blistering, or checking after 100 hours in distilled water at 100°F.
	No cracking or loss of adhesion when deformed 180° over conical mandrel (maximum elongation of 26%).
	Not applicable.
	Not applicable.

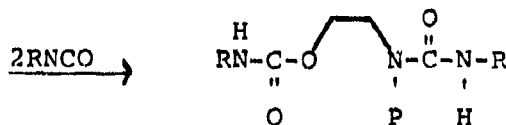
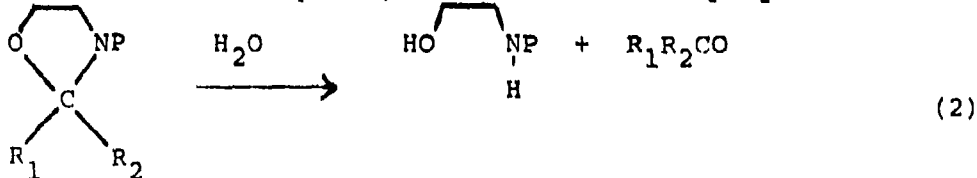
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anate terminated prepolymers (polyisocyanates) to form a polyurethane.



The polyol and polyisocyanate may be formulated into a two-component coating formulation. One limitation of this type of system is the short pot life (particularly when a catalyst is used).

An additional approach to two-component coatings systems is based on blends of a polyfunctional oxazolidine with isocyanate. Properly chosen oxazolidines are weak bases, have no active hydrogen, and when reacted with water are rapidly converted to the parent alkanolamine which reacts with a polyisocyanate to form an excellent coating. The chemistry of the oxazolidine ring is such that it may be conveniently introduced into a variety of polyfunctional and polymeric matrices.



P = Polymeric Substrate

Acryloid AU-568, an oxazolidine from Rohm and Haas Company (originally supplied as experimental resin QR-568), was evaluated for incorporation into high solids coating systems. Because the reaction of the oxazolidine with water forms the alkanol-

amine, the Acryloid AU-568 was screened with the polyols also being evaluated.

### C. Summary of Initial Contract

The first phase of the original contract was directed toward the analysis of viscosity-concentration profiles and the effect of high shear rates on the viscosities of polymer/solvent combinations. From the data obtained, methyl ethyl ketone (MEK) was found to be the solvent of choice in these high solids coatings because of its effectiveness in lowering the viscosities of the polymer solutions.

As measured with high shear instrumentation, the viscosities of these high volume solids oligomer solutions exhibit a reversal in their rheological properties relative to the viscosities obtained at low shear rates and low volume solids. Although the possibility exists that a certain degree of this reversal may be due to an artifact of the instrumentation, a trend toward pseudoplasticity at high shear for these high volume solids oligomer is clear.

The formulator of high volume solids coatings should be cautious in choosing a given system based simply on low shear viscosity measurements. If the present data is indicative of the true behavior of these solutions, the rheological characteristics of high solids systems may lie on a serpentine viscosity-concentration profile display, and the specific behavior for a desired application must be considered before a system selection is made.

The second phase involved the evaluation of clear films.

The unpigmented polyols, formulated with isocyanate crosslinking agents, were qualitatively assessed to obtain their spray properties and tested for final film properties. Three polyols, Acryloid AU-568, an oxazolidine (Rohm and Haas Company), Cargill 5760 (Cargill, Inc., Chemical Products Division), and NIAX PCP-0300 (Union Carbide) were selected for continued evaluation and formulation optimization.

The three polyols identified in the second phase for further evaluation, were pigmented with titanium dioxide, and with Desmodur N-100 (Mobay Chemicals), and evaluated for physical and chemical properties during the third phase. Good fluid resistance properties were maintained when these systems were pigmented, but the low temperature flexibility performances were degraded.

The final phase of the program consisted of blending the various components previously evaluated to achieve a formulation which closely approximates the program goals as specified in Mil-C-83286B.

As a final result, one formulation (2408-9) a blend of Acryloid AU-568, NIAX PCP-0300, and Desmodur N-100, was developed. This formulation was found to exhibit performance properties closely approximating the program goals (Tables 2 and 3).

Table 2  
Formulation 2408-9 Composition

<u>Material</u>	<u>Weight Percent</u>	<u>Volume Percent</u>
TiO <sub>2</sub>	20.93%	6.40%
Acryloid AU-568	17.74	19.95
NIAX PCP-0300	5.91	6.47
Desmodur N-100	34.05	35.63
MEK - Urethane Grade	20.79	31.00
Dibutyl tin dilaurate (1% in MEK solution)	0.58	0.55
PVC = .10%		
NCO/OH = 1.77		



Table 3

Performance Properties of Formulation 2408-9

Composition	Acryloid AU-568/NIAX PCP-0300/Desmodur N-100
Viscosity (#2 Zahn Cup)	23 seconds
Spray Characteristics	Sprays well with slightly coarse atomization-good leveling.
Impact Flexibility	40% (60) <sup>a</sup>
High Temperature Stability-Impact Flexibility	40% (60) <sup>a</sup>
Low Temperature Flexibility-Straight Mandrel	25.4 mm (25.4 mm) <sup>a</sup>
60° Gloss	93 (90) <sup>a</sup>
5% Salt Spray Resistance	No effect
100% Relative Humidity	No effect
Accelerated Weathering	No effect
Fluid Resistance:	
Lubricating Oil (24 hrs at 250°F)	1 <sup>b</sup> (1) <sup>a</sup>
Hydraulic Fluid (7 days at 77°F)	0 <sup>b</sup> (1) <sup>a</sup>
Hydrocarbon Fluid (7 days at 77°F)	0 <sup>b</sup> (1) <sup>a</sup>
Skydrol 500B Fluid (7 days at 77°F)	0 <sup>b</sup> (2) <sup>a</sup>
Distilled Water (4 days at 100°F)	1 <sup>b</sup> (1) <sup>a</sup>

a. Program goals

b. Degree of softening as indicated by the decrease in pencil hardness units.

The research effort of the present contract followed two approaches. The first was to further evaluate and upgrade formulation 2408-9. The second was to continue to evaluate new commercially available resins as potential candidates for high solids systems.

## II. Results and Discussion

### A. Continued Evaluation of Formulation 2408-9

Intensified evaluation of formulation 2408-9 indicated that several areas existed in which the formulation did not meet the program goals. The polyol component (polyol, oxazolidine, pigment blend) was found to be unstable during storage, increasing in viscosity with passing time. The pot-life of the fully blended formulation was shorter than the two hour requirement. (For the purpose of this program, pot-life has been defined as the amount of time during which the viscosity will double). The flexibility performances, although close, did not fulfill the requirements for room temperature impact and high temperature stability. Also, varying degrees of foaming and sagging were occasionally noted to occur within the formed films. Studies, designed to find solutions to these problems, were carried out.

#### 1. Long-Term Stability of the Polyol Component

##### a. At Ambient Temperatures

During a preliminary stability study, samples of a polyol-oxazolidine mixture in a 1:3 ratio were prepared. To one sample, triethyl amine (TEA) was added in an effort to retard the ring opening reaction of the oxazolidine. It has been reported<sup>2</sup> that the more basic the ring nitrogen of the oxazolidine, the slower the rate of hydrolysis. Using a Brookfield Synchro-Lectric Viscometer, the viscosities of the two mixtures were monitored for 26 days.

Both formulations exhibited increasing viscosities (Figure 1).

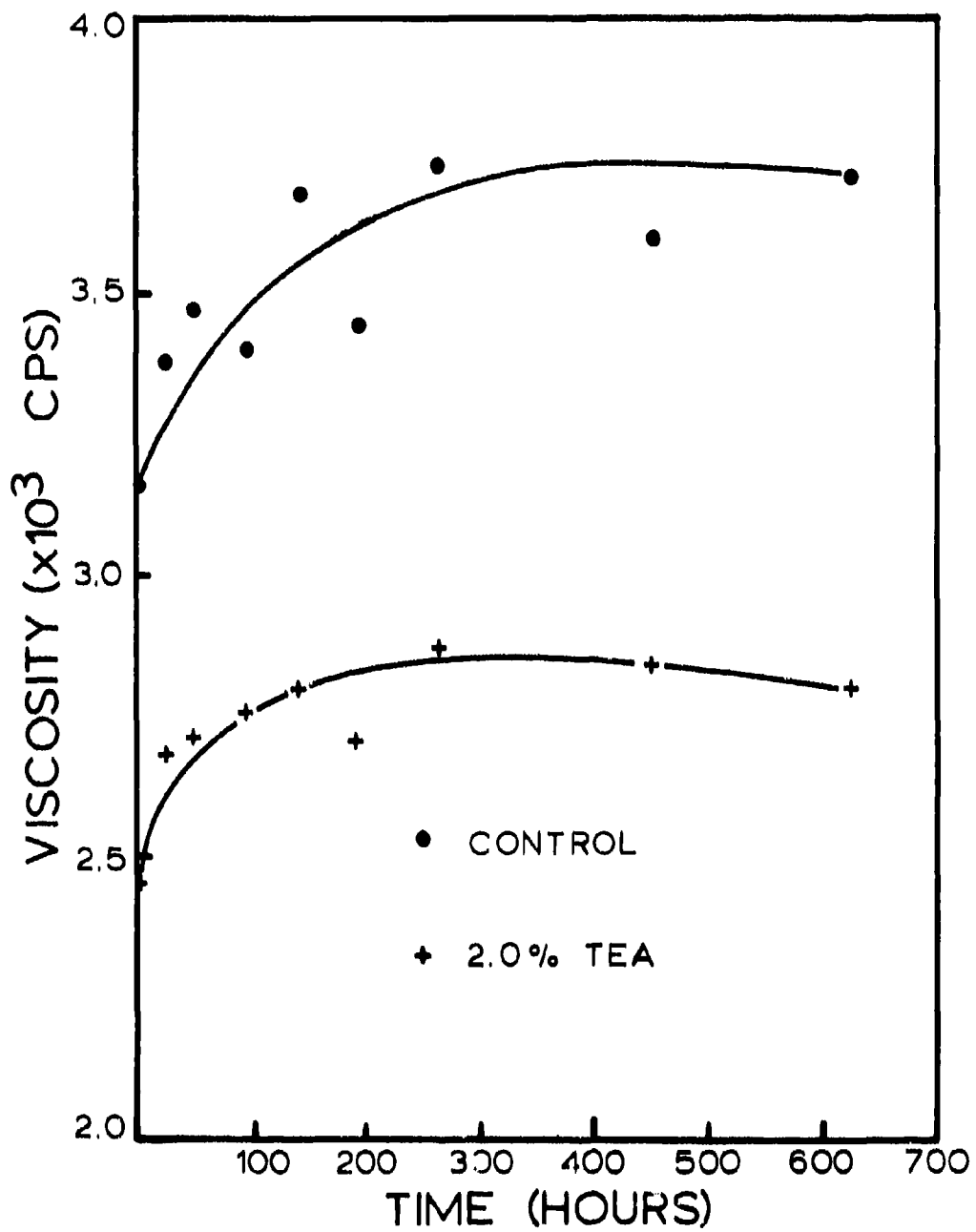


Figure 1. Effect of TEA Addition on Viscosity of Polyol-Oxazolidine Mixtures

After 14 days the viscosities achieved constant values. The mixtures incorporating the amine exhibited lower viscosities as well as slower viscosity increases. It should be noted that in both cases, the viscosity increases were not extremely high. These results indicate that the possibility of any extensive ring opening reaction occurring is remote. A study of the stability of pigmented oxazolidine-polyol mixtures was then initiated.

Up to this point of the research effort, practice had been to prepare the pigment grinds in a pebble mill incorporating a portion of the oxazolidine component with the pigment. The remaining materials were then added, mixed, and the resulting formulation was applied and tested. To obtain the program goal of a two-package system and determine the long term shelf stability of the pigment grinds, all three components; oxazolidine, polyol, and pigment were ground together using a high speed dispersator (HSD). A portion of the grind was treated with TEA. (In order to maintain a pot-life comparable to the non-amine containing systems continuing the catalyst dibutyl tin dilaurate (DBTDL), the level of amine incorporated was lower than that used in the unpigmented polyol-oxazolidine mixtures.) The grinds were stored at room temperature and checked at weekly intervals for viscosity and pigment settling. Each time the grinds were checked, a portion was removed and blended with a mixture of isocyanate and solvent to complete the formulation. The viscosity of the completed formulation was 24-25 seconds

(#2 Zahn Cup). Both grinds attained the same constant level of viscosity after four weeks, although the amine containing grind had a lower initial viscosity (Figure 2).

Pigment settling which could not easily be redispersed with a spatula, was not noted in any of the grinds. The spray coated panels did not exhibit any visible defects and were identical to those incorporating freshly prepared pigment grinds.

The overall coating properties of the DBTDL and TEA catalyzed formulations were identical. Following one week of storage, when the grind was blended into the formulation, the hardness of the resultant coating had decreased one pencil hardness unit. Further storage did not affect the film hardness.

Room temperature impact flexibility and low temperature flexibility properties exhibited some deterioration when the fully formulated system was prepared with an aged grind. This is in comparison to a formulation incorporating a freshly prepared pigment grind. The reduction in the flexibility properties may result from moisture contamination. The presence of excessive moisture within the formulation would not only open the oxazolidine ring, but would consume the isocyanate fraction which would otherwise be available for chain propagation reactions.

#### b. At Elevated Temperatures

The stability of the pigment grind at elevated temperatures (53.9°C) was also determined. The coating properties of the fully formulated system incorporating an aged pigment grind

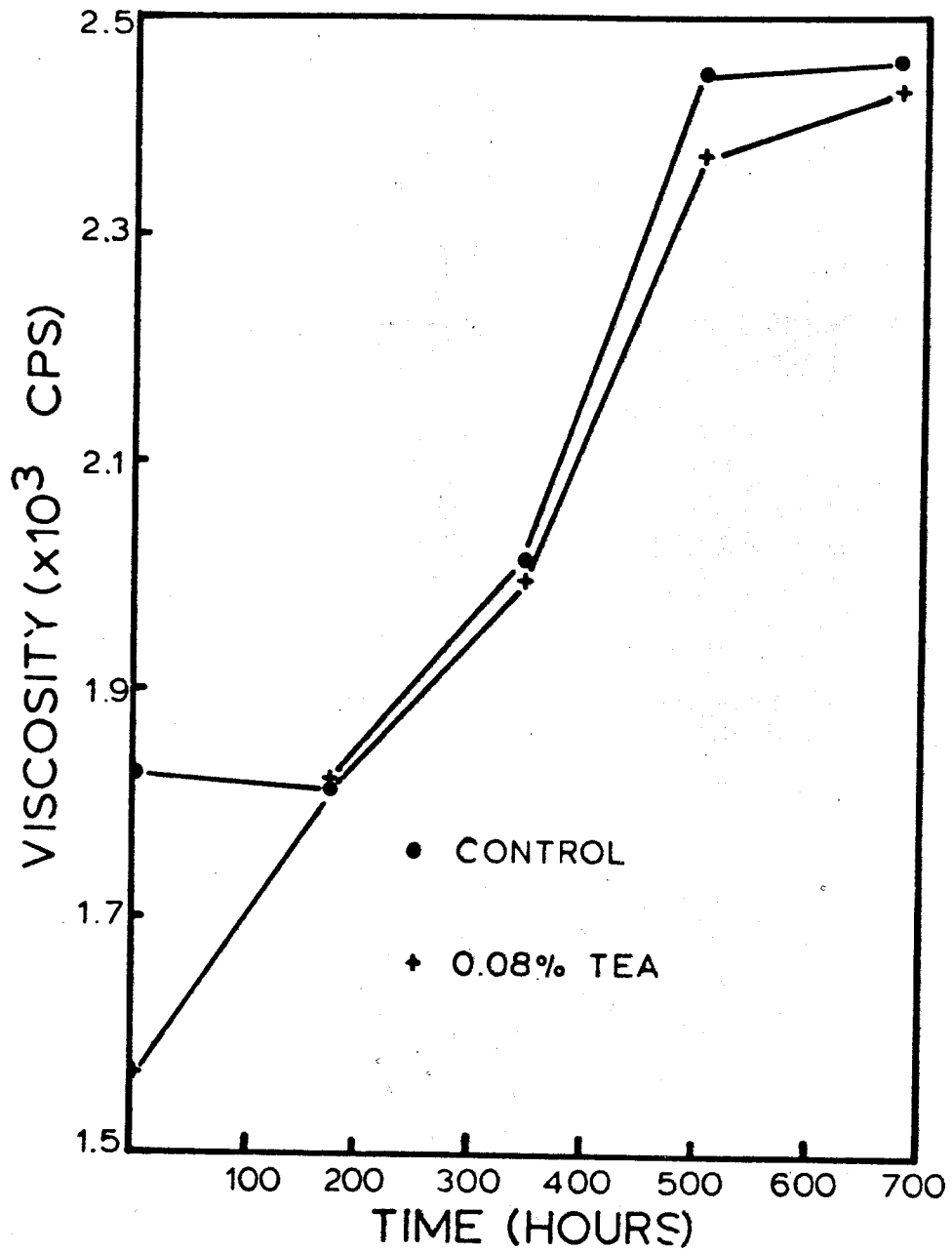


Figure 2: Effect of TEA Addition on Viscosity of Polyol-Oxazolidine Pigmented Mixtures

were also determined. More than a two fold increase in viscosity (Table 4) was noted in the Acryloid AU-568/NIAX PCP-0300/TiO<sub>2</sub> pigment grind over a period of 20 days. The complete formulations were also of high viscosity (at 65% volume solids) as compared to formulations prepared from grinds aged at room temperature. Also, the pot-lives exhibited a small decrease (Figure 3).

Table 4

Effect of High Temperature (53.9°C) Aging on the Viscosity of Pigment Grinds

<u>Pigment Grind</u>	<u>Brookfield Viscosity at 50 RPM with #4 Spindle, cps</u>
AU-568/PCP-0300/TiO <sub>2</sub> <sup>a</sup>	
Control (20 days at 25°C)	1480
Aged (20 days at 53.9°C)	3480
AU-568/Cargill 5770/TiO <sub>2</sub> <sup>b</sup>	
Control (20 days at 25°C)	1300
Aged (20 days at 53.9°C)	4850

- 
- a. Composition (% by weight): TiO<sub>2</sub>: 45.2, Acryloid AU-568: 37.9  
NIAX PCP-0300: 1.31, MEK: 3.8
- b. Composition (% by weight): TiO<sub>2</sub>: 45.4, Acryloid AU-568: 38.1  
Cargill 5770: 12.7, MEK: 3.8<sup>2</sup>

The high temperature aging (53.9°C) of the pigment grind did not significantly alter the coating properties of the films resulting from the complete formulation (Table 5). Aging at elevated temperatures appears to have improved the impact flexibility slightly, possibly due to a reduction in the glass transition

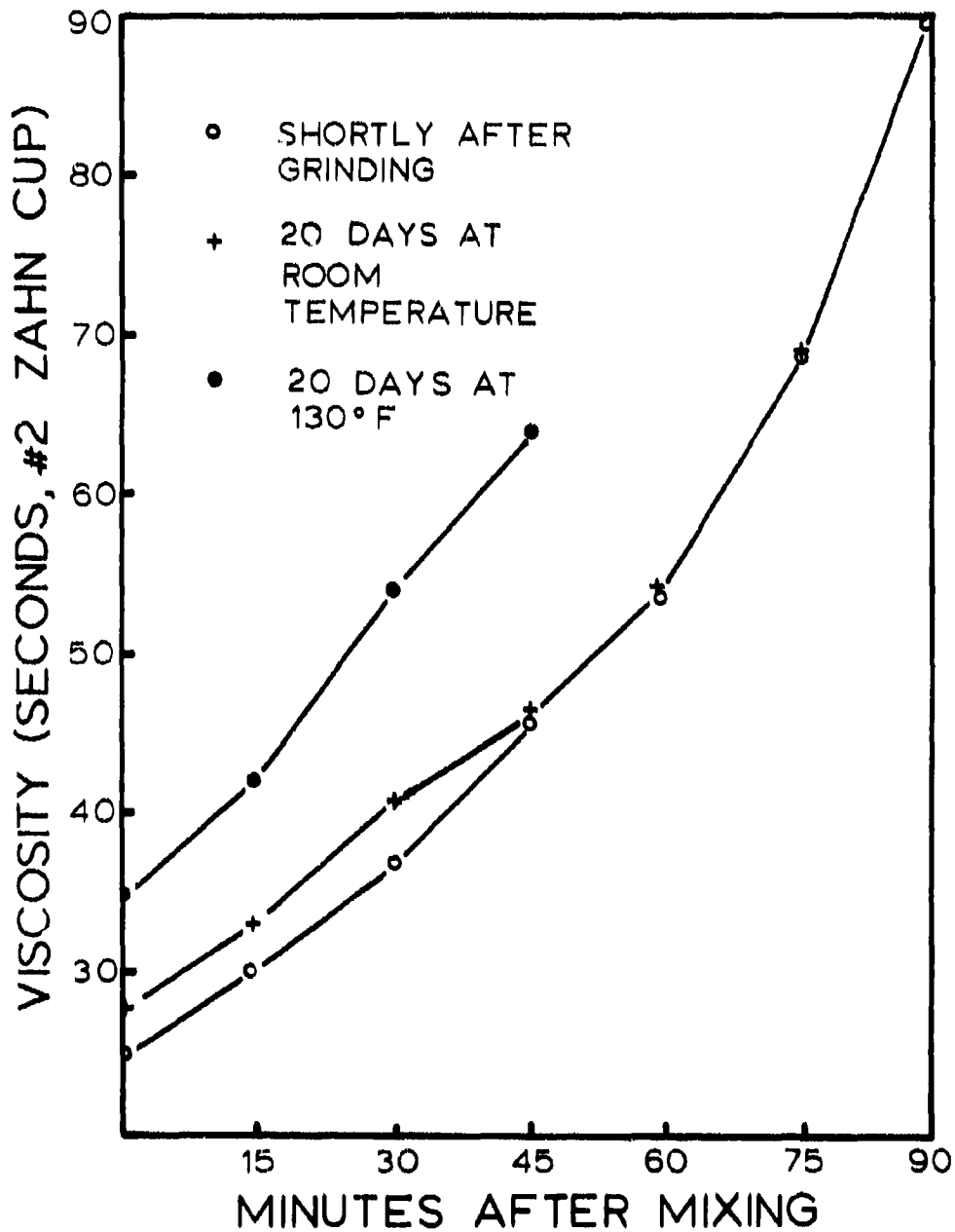


Figure 3: Effect of Accelerated Aging on Pot-life of Acryloid AU-568/NIAX PCP-0300/TiO<sub>2</sub> Grind



TABLE 5

Effect of Accelerated Aging of Pigment  
Grind on Coating Properties

Properties	AU-568/PCP-0300/Des N-100		AU-568/Cargill 5770/L-2291	
	Control <sup>a</sup>	Aged <sup>b</sup>	Control <sup>a</sup>	Aged <sup>b</sup>
Gloss at 60°	92.2	92.6	92.9	93.2
Hardness, Pencil	HB	HB	HB	HB
Impact Flexibility at Room Temperature (%)	20	60	20	40
Low Temperature Flexibility, mandrel passed (mm)	25.4	25.4	25.4	25.4
Solvent Resistance Lube Oil, 24 hr at 250°	HB	HB	HB	HB
Water, 96 hr at 100°F at R.T.	HB	HB	HB	HB
Skydrol 500B, 168 hr.	HB	HB	HB	HB
Type III solvent, 168 hr at RT	2B	2B	2B-3B	<4B
Hydraulic Fluid 168 hr at RT	HB	HB	HB	HF
Glass Transition Temperature of cured film	31	18	32	27

a. 20 days at Room Temperature

b. 20 days at 53.9°C

temperature (Tg) of the cured films.

A pigment grind made from  $\text{TiO}_2$  and the oxazolidine oligomer only, was also aged at  $53.9^\circ\text{C}$  to determine if the viscosity rise was due to an interaction between the oxazolidine oligomer and the polyhydroxy compound (NIAX PCP-0300). In this study, the viscosity of the grind and the pot-life of the complete formulation were determined at regular intervals. The results are presented in Table 6 and figure 4. In this system, a more than two-fold increase in the viscosity of the grind was noted after 12 days of aging. This rules out the possibility of an oxazolidine polyol interaction as the main reason for the viscosity rise. One of the reasons may be that the opening of the oxazolidine ring is accelerated during aging at high temperatures.

TABLE 6

Effect of Accelerated Aging on the Viscosity  
of a Pigment Grind\* ( $\text{Acryloid AU-568/TiO}_2$ )

Number of days at $53.9^\circ\text{C}$	Brookfield Viscosity at 50 RPM with #4 Spindle, cps
0	1360
6	1920
12	3020

\*Composition (% by weight);  $\text{TiO}_2$ : 45.2, Acryloid AU-568: 51.0  
MEK: 3.8

2. Pot-life Study

a. Catalyst Variation Study

Using a #2 Zahn cup, the viscosity of the fully blended

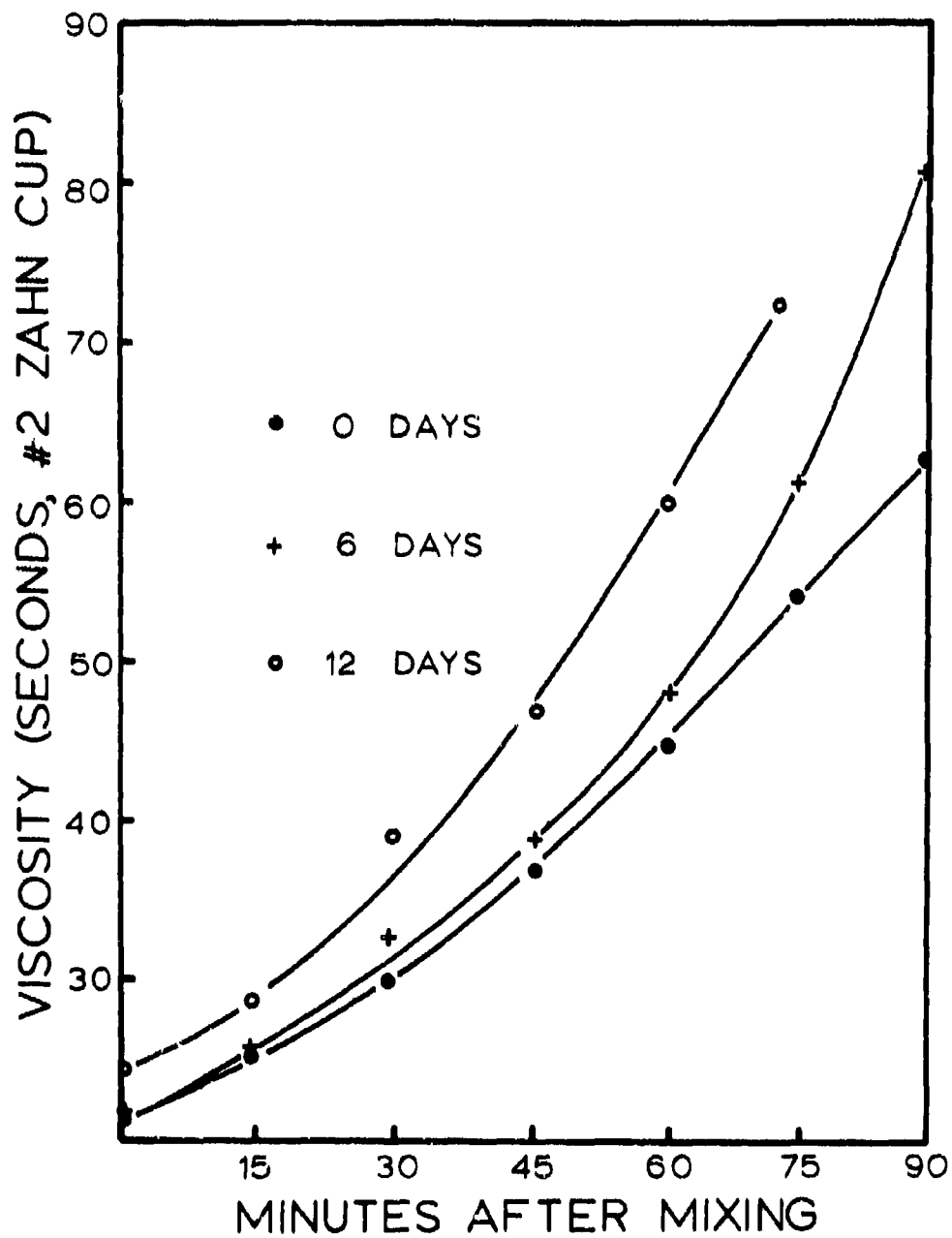


Figure 4: Effect of Accelerated Aging on Pot-life of Acryloid AU-568/TiO<sub>2</sub> Grind Mixed with Desmodur N-100

formulation 2408-9 was measured every 15 minutes over a period of two hours (the minimum pot-life required by Mil-C-83286B). The data accumulated in this study showed that the viscosity increased exponentially with time (Figure 5). Thirty minutes after mixing, the viscosity was no longer within the range of conventional air spray equipment. As the viscosity increased, atomization became coarse and eventually non-existent.

A study was carried out to determine if the pot-life could be lengthened by varying the level of the catalyst. Formulations containing 0, 25, 50, 75, and 100 percent of the catalyst level of formulation 2408-9 were prepared and evaluated for pot-life and coating performance properties.

The varying levels of catalyst did not result in obvious differences in performance properties of the coatings. However, at the 0 and 25 percent catalyst levels, a direct increase in viscosity with respect to time was noted (Figure 5). In the two hour period, these formulations doubled in viscosity. The formulations at higher catalyst levels exhibit a ten-fold viscosity increase during the same time period.

#### b. Effects of Additives

One of the major concerns in oxazolidine containing formulations is moisture contamination. The higher the water content of the formulation the shorter is the pot-life. It was noted that an addition of a small amount of water (0.5% by weight) would cause complete gelation in less than thirty minutes

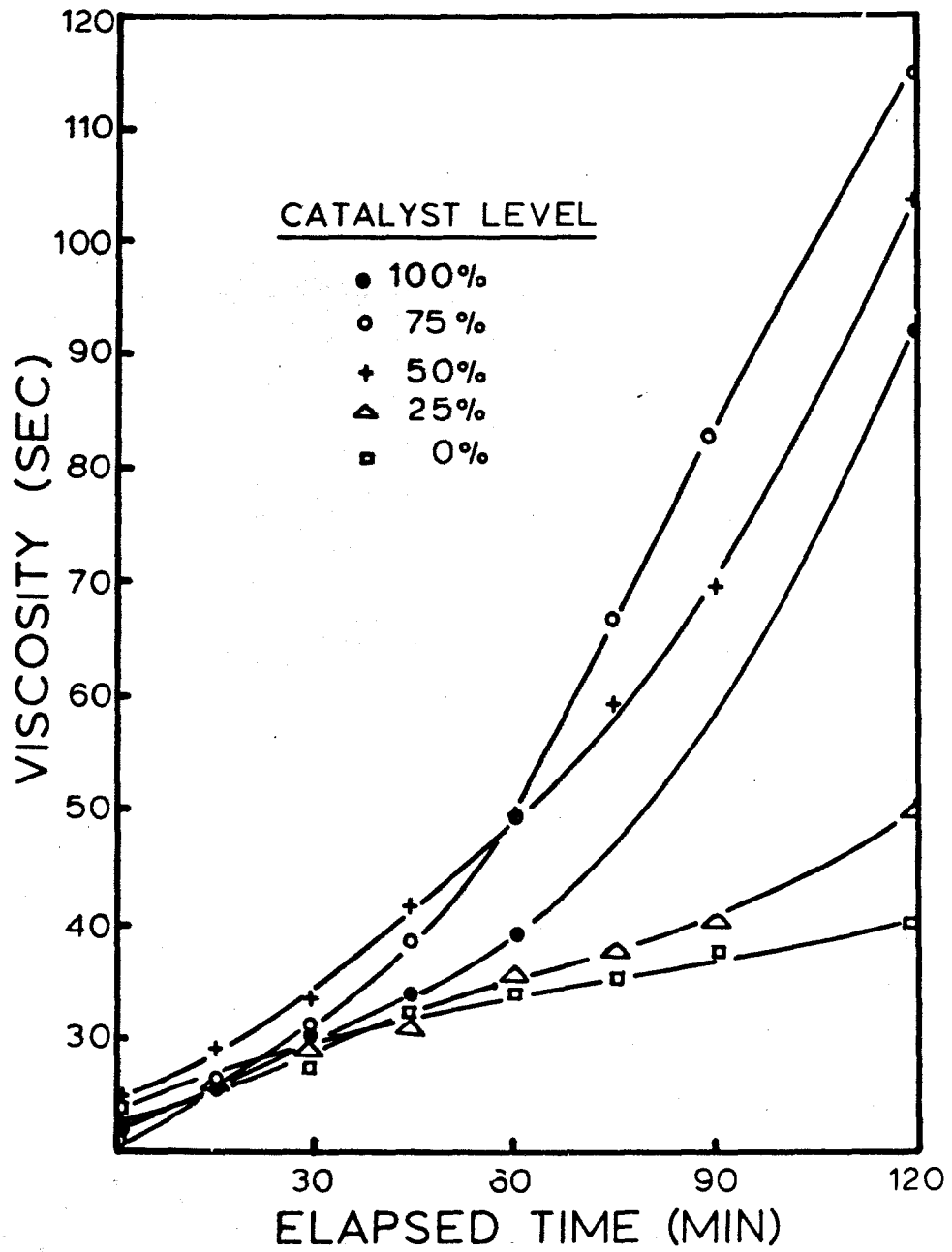


Figure 5: Formulation 2408-9 Catalyst Variation Study

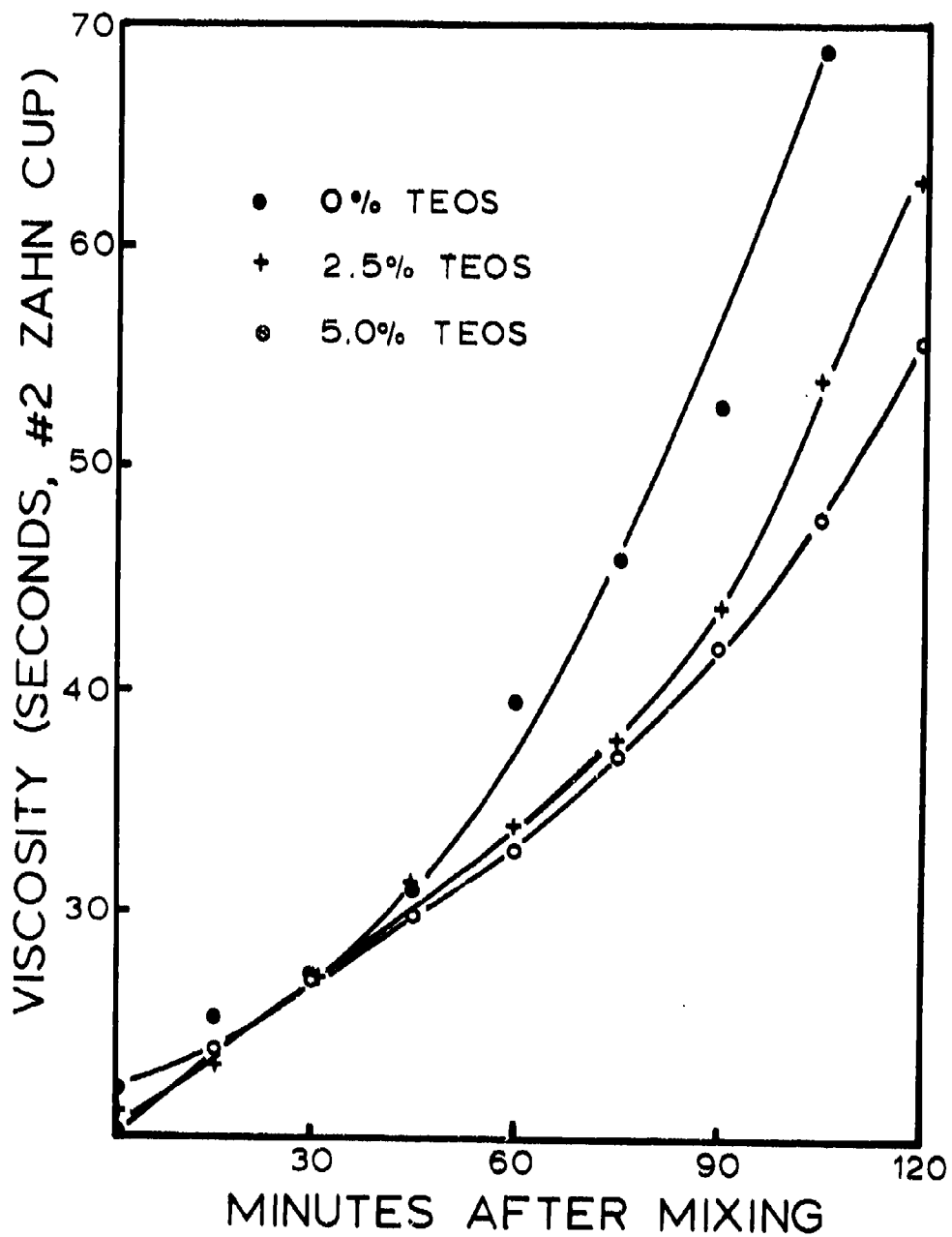


Figure 6: Effect of Tetraethylorthosilicate (TEOS) on Pot-life of Acryloid AU-568/NIAX PCP-0300 System mixed with Desmodur N-100

after mixing with the isocyanate component. To avoid this situation, the use of a moisture scavenger additive was investigated.

Of the additives evaluated, tetraethylorthosilicate (TEOS) was noted to extend the pot-life an additional thirty minutes when used at a level of 2.5% by weight (Figure 6). The use of TEOS did not affect the drying times or any of the performance properties.

A study evaluating the effect of adding TEOS and TEA to the formulations with respect to long-term stability of the polyol component was performed. Three sets of test samples were prepared as indicated in Table 7. One set of grind samples was blended into the topcoat formulation and evaluated for pot-life. The remaining sets were stored, one at room temperature and the other at elevated temperatures (37.4°C) for 68 days. At the end of this time period, the grind samples were evaluated for pigment settling and blended into the test formulation.

Both the TEA and TEOS containing formulations exhibited pot-lives longer than the control sample before and after aging. The samples stored at elevated temperatures exhibited high initial viscosities and rapid viscosity increases indicating poor long term stability (Figures 7, 8, & 9).

The TEOS samples stored at room temperatures exhibited pot-lives longer than those samples tested immediately after preparation (Figure 10). The extension of pot-life is probably

Table 7

Effect of Additives on Long Term Stability Grind Compositions<sup>a</sup>

Material	Formulation				
	A	B	C	D	E
TiO <sub>2</sub>	44.88	44.14	44.70	43.99	44.15
AU-568	37.56	36.49	37.41	36.82	36.94
PCP-0300	13.04	12.66	12.98	12.77	12.82
U.G. MEK	4.44	3.62	3.73	3.60	3.67
DBTDL (1% in MEK)	--	1.18	1.18	1.18	1.18
TEA	0.08	--	--	--	--
TEOS	--	2.41	--	1.82	1.21

a. Percent composition by weight



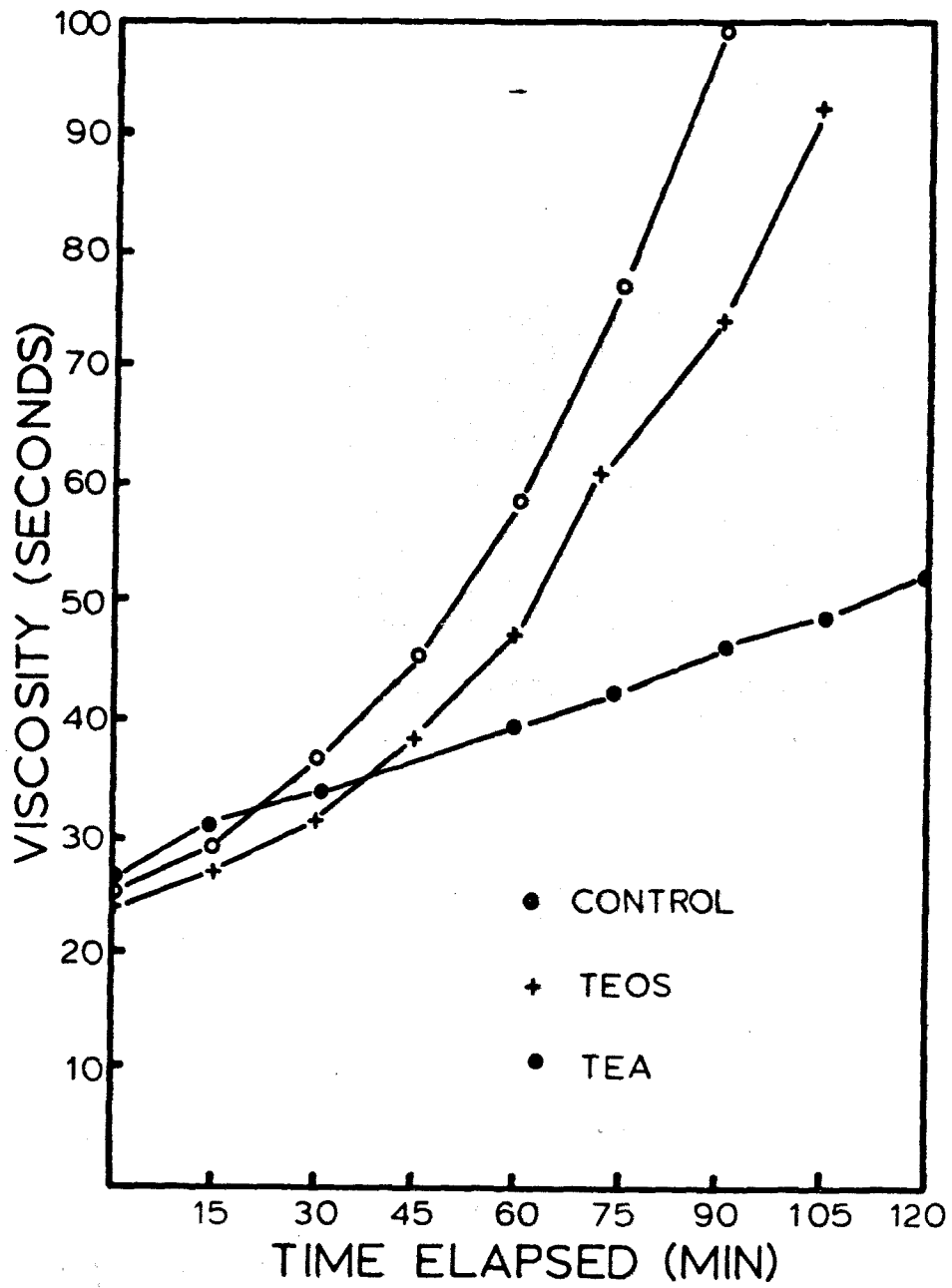


Figure 7: Effect of Additives on Pot-life of AU-568/  
 NIAx PCP-0300 Grind (immediately after preparation)

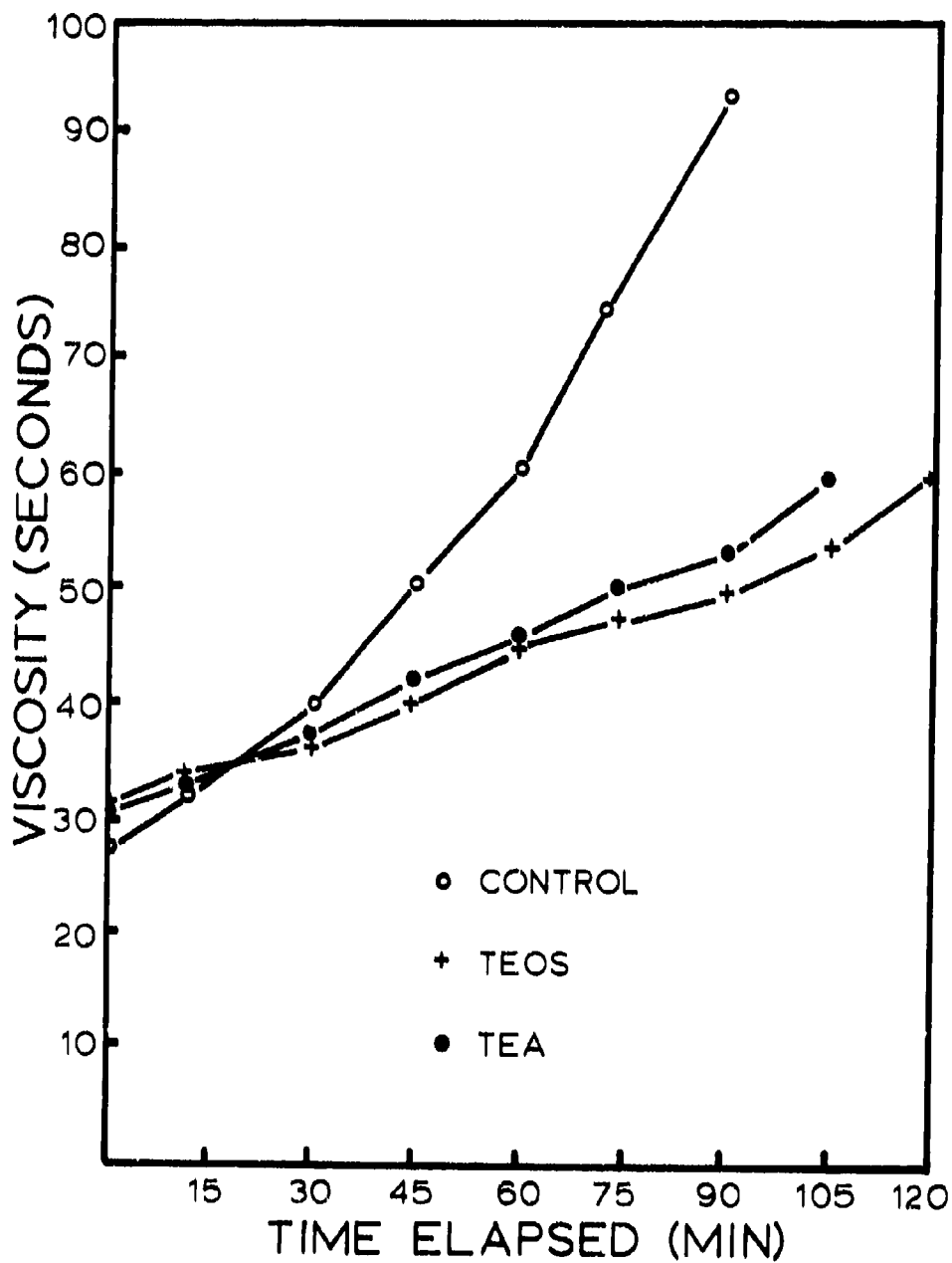


Figure 8: Effect of Additives on Pot-life of AU-568/  
 NIAX PCP-0300 Grind (stored 68 days at 77°F)

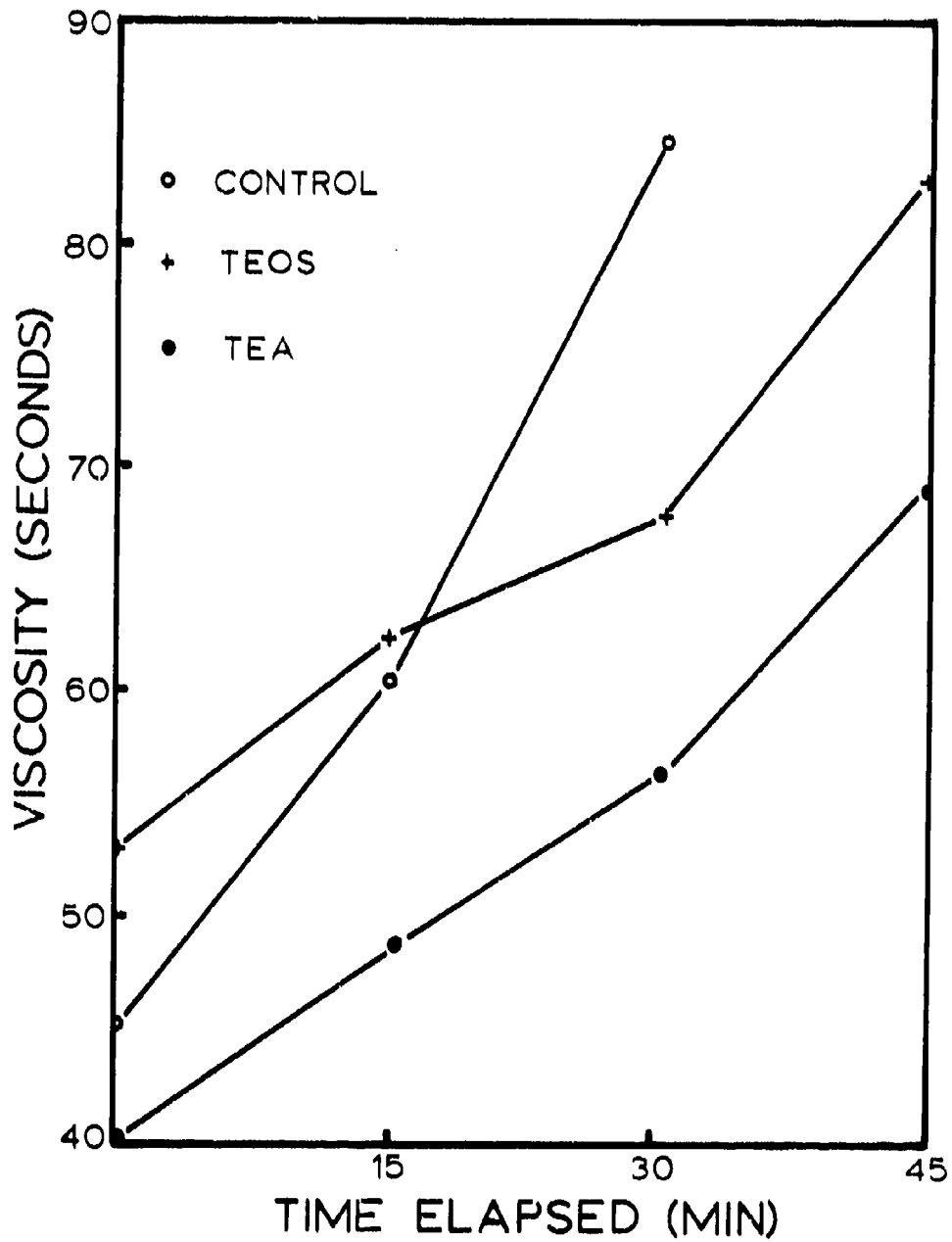


Figure 9: Effect of Additives on Pot-life of AU-568/  
 NIAX PCP-0300 Grind (stored 68 days at 100°F)

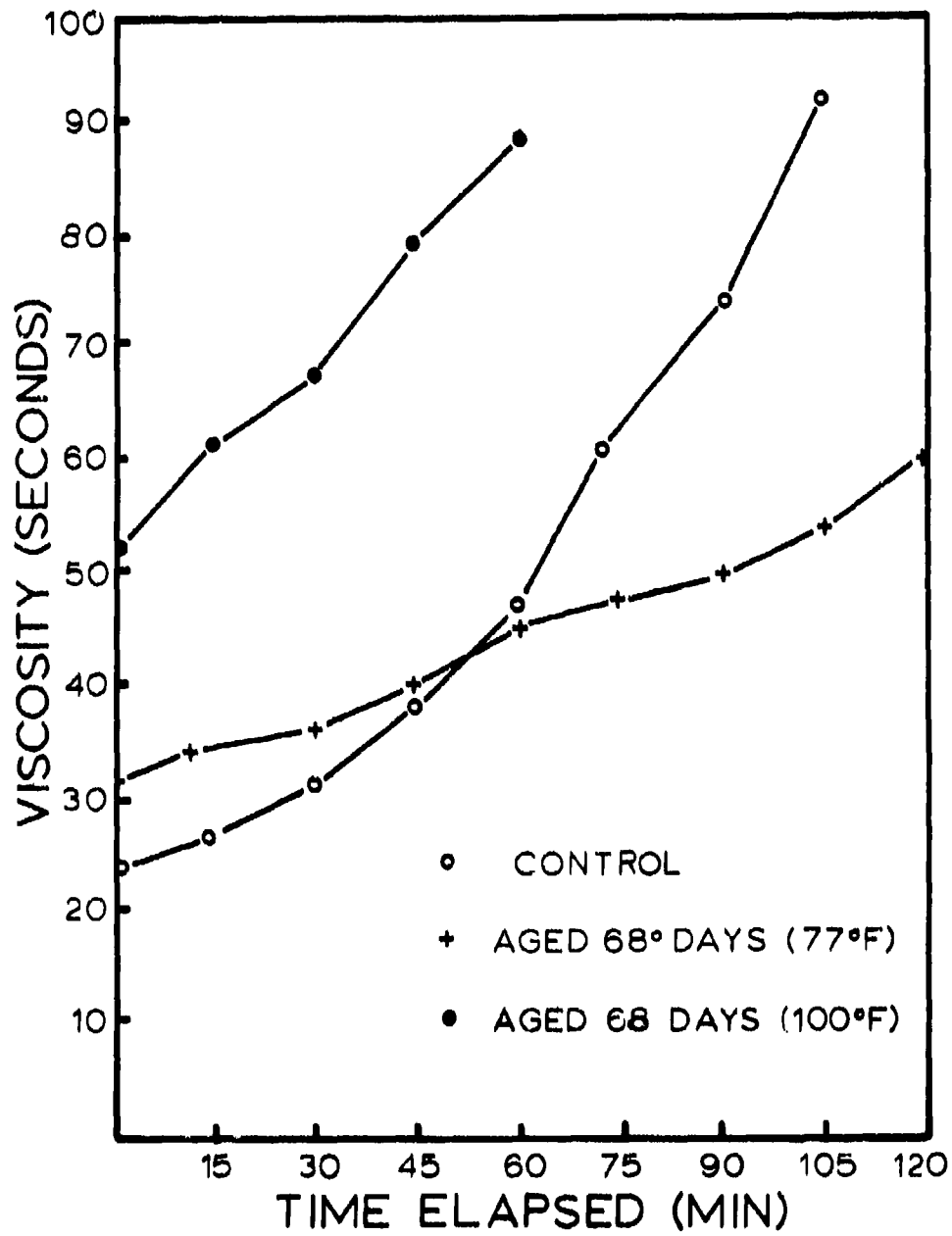


Figure 10: Effect of TEOS on Pot-life After Storage

due to the fact that during storage, the TEOS (a moisture scavenger) had a longer time to react.

After storage, all of the samples exhibited some degree of pigment settling and needed to be shaken mechanically to effect redispersion. The grinds incorporating TEOS appeared to be approaching a gel-like condition. This was much more evident in the grinds stored at elevated temperatures.

#### c. Comparison of Raw Materials

To insure reproducibility of the performance properties exhibited, and initiate quality control of the raw materials, analyses for non-volatiles, water, amine, hydroxy, and acid values were performed when appropriate. Each sample of the raw materials was analyzed and then used to prepare formulation 2408-9. The formed films were evaluated for chemical and physical performance properties.

From the results obtained (Table 8), it was noted that the three batches of Acryloid AU-568 did not vary significantly from one to another. However, the older sample of NIAX PCP-0300 was found to contain 3.5 times the amount of water as that in a more recently received sample and was cloudy in appearance. All other physical characteristics were similar. Formulations incorporating the newer polyol exhibited viscosities which increased at half the rate of those prepared with the older polyol. By using the more recently received polyol, the pot-life of formulation 2408-9 was significantly improved.

TABLE 8

Analysis of Raw Materials

<u>Sample</u>	<u>%NVM (2 hrs, 105°C)</u>	<u>Water (Via K-F) Titration</u>	<u>Amine Equiv.</u>	<u>Acid Equiv.</u>	<u>*Hydroxyl Value</u>
<u>Acryloid AU-568</u>					
1. Lot 2-3496	85.9		1.58 meq/g		
2. Lot 2-0576	84.7		1.50 meq/g		
3. Lot 2-3463	87.7		1.61 meq/g		
<u>NIAX PCP-0300</u>					
1. 2442-126E	98.5	0.04		<u>0.10mg KOH</u> g	<u>314mg KOH</u> g
2. N-98085 (cloudy)	98.6	0.14		<u>0.10mg KOH</u> g	<u>342mg KOH</u> g

\*Pyromellitic Dianhydride Method  
Catalyzed with Imidazole

Analysis of the titanium dioxide R-960.09 (E.I. DuPont de Nemours Co.) used to pigment the high solids system, indicated the presence of one percent (by weight) of volatile materials as determined by ashing. Formulations were made in which the pigment was used as supplied and after being dried overnight at high temperatures. Evaluation of the formulations' pot-lives and performance properties of the coatings indicated no difference between the two pigments.

d. Effect of Volume Solids on Pot-life

In addition to moisture contamination, higher volume solids (65%) was also found to be responsible for shortened pot-life. To demonstrate the effect of percent volume solids on pot-life, a number of pot-life determinations were made at different percent volume solids levels. As presented in Figure 11, the viscosity of the complete formulations at high volume solids increased at rates

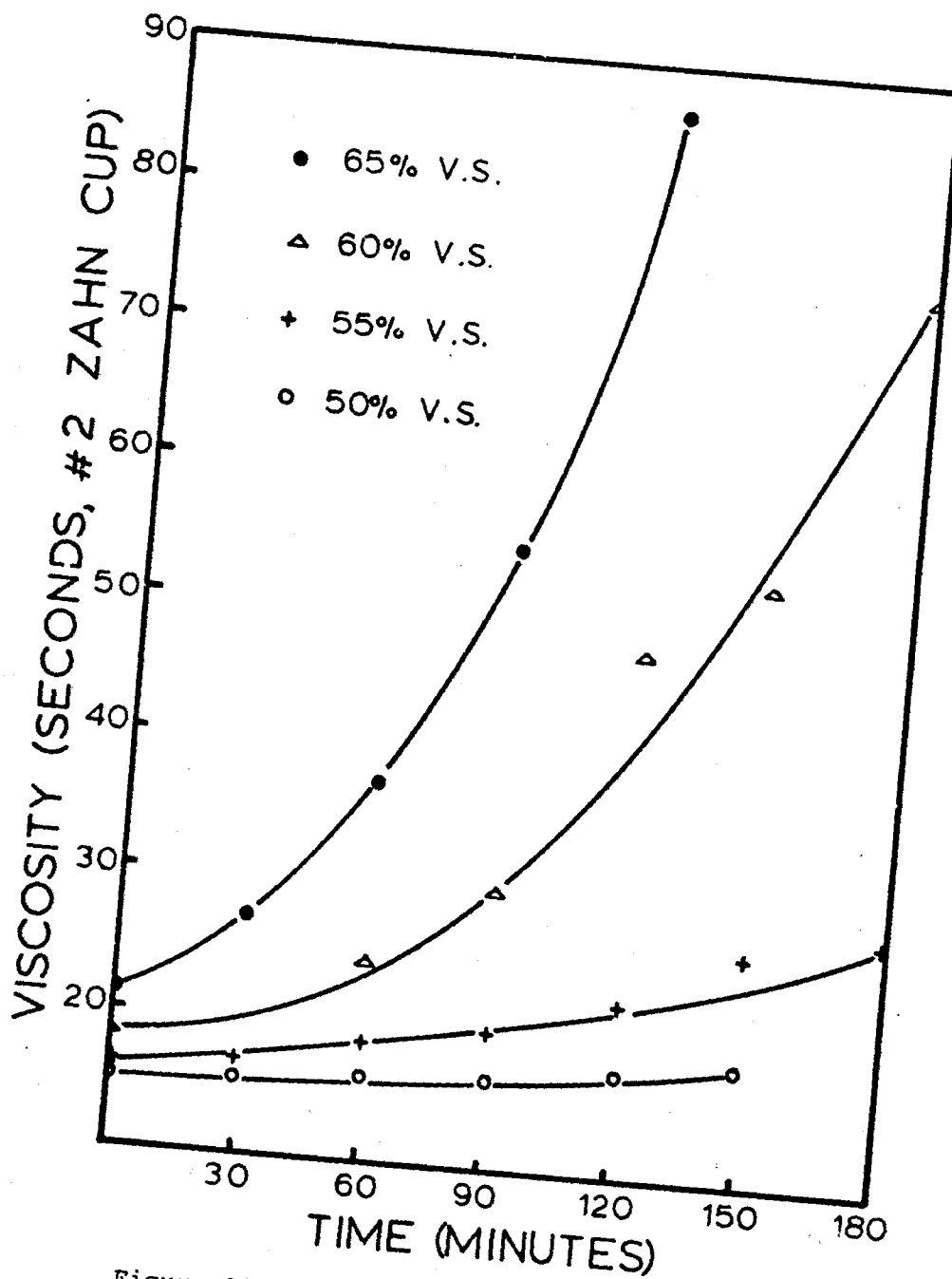


Figure 11: Pot-life of Formulation 2408-9 at Varying Volume Solids

faster than those at lower volume solids. It was also noted (Figure 12) that the decrease in pot-life with decreasing percent volume solids was quite rapid in the range studied. Thus, it appears that although the oxazolidine containing formulations are susceptible to moisture contamination, another reason for the short pot-life was the high volume solids of the complete formulations.

### 3. Flexibility Properties

The flexibility performances (room temperature impact flexibility, high temperature stability, and low temperature flexibility) of formulation 2408-9 have been less than acceptable. Two approaches to improve these properties were taken. In the first approach, ten percent of the Acryloid AU-568 was replaced with QM-562 (a flexibilizing agent for Acryloid AU-568, manufactured by Rohm and Haas). The second approach involved replacing ten percent of the Desmodur N-100 weight fraction of the formulation with General Mill's DDI 1410, a diisocyanate. It was theorized that the incorporation of a diisocyanate would increase the flexibility by decreasing the amount of cross-linking within the formed films. Evaluation of the performance properties of the films prepared according to the two approaches, indicated no improvement in the flexibility properties.

### 4. Foaming and Sagging

An experiment, designed to determine if a correlation exists between film thickness and the amount of foaming and



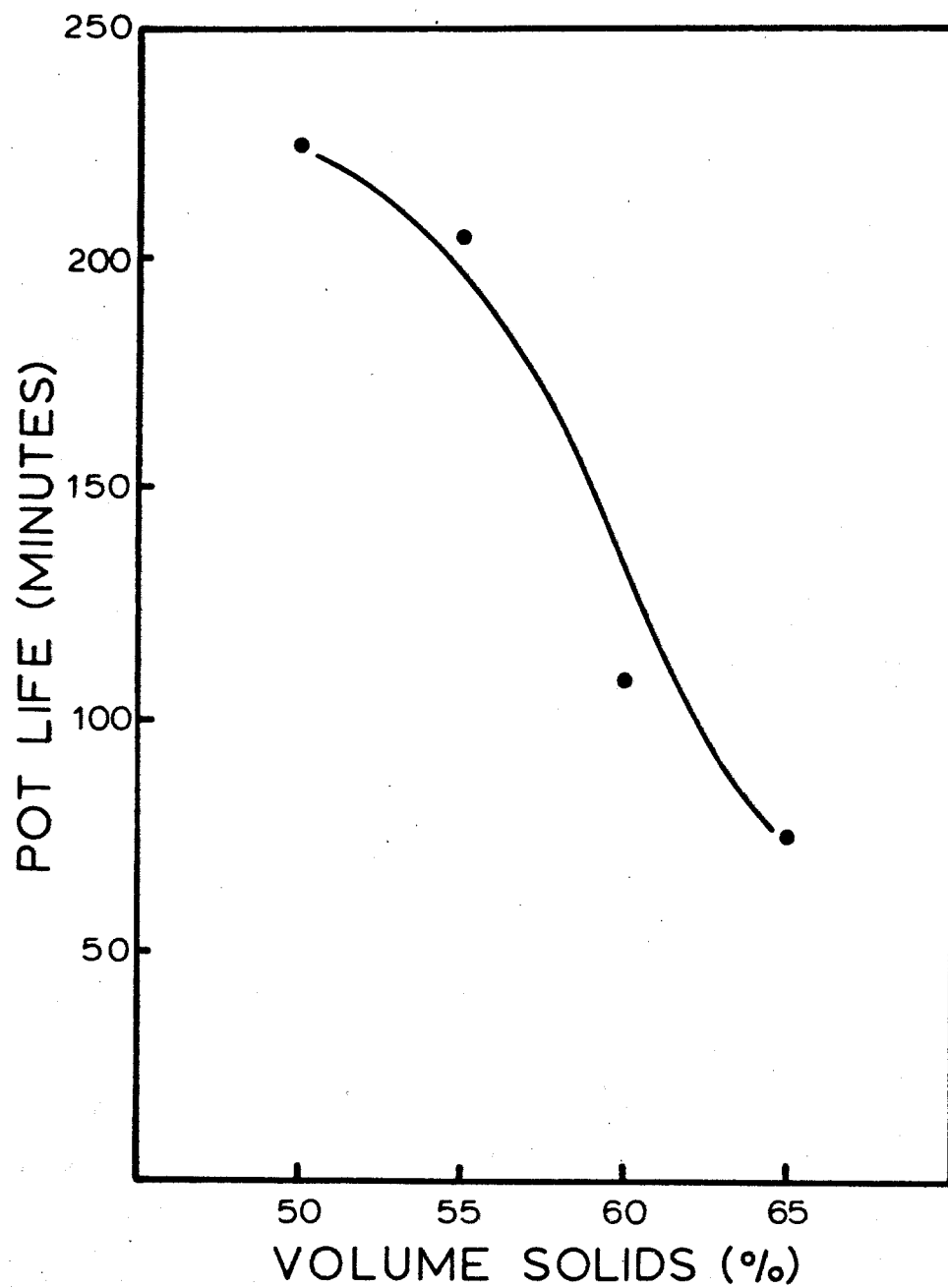


Figure 12: Pot-life (time) vs. Volume Solids of Formulation 2408-9

sagging within the films, was performed. Using a drawdown bar, films of varying thicknesses were applied to unprimed aluminum test panels. After seven days cure at ambient conditions, the films were judged for the amount of foaming and sagging. Small bubbles were found to appear when the dry film exceeded 50.8 mm (2.0 mil). After this point, the foaming and sagging increased with increasing film thickness.

#### 5. Correlation between Coating Formulations and Properties

In order to develop formulations with predictable final properties, a correlation between the composition of the final formulations and the corresponding coating properties was attempted. A stepwise regression analysis of the data on the compositions (variables) and corresponding coating properties (responses) was made. For the sake of simplicity and because of previous encouraging test results, only the Acryloid AU-568/NIAX PCP-0300/TiO<sub>2</sub>/Desmodur N-100 formulations' data at 65 percent volume solids and 10 percent pigment volume concentration were selected for analysis.

The four independent variables selected were concentrations of catalyst ( $X_1$ ), Acryloid AU-568 ( $X_2$ ), NIAX PCP-0300 ( $X_3$ ), and the ratio ( $X_4$ ) of isocyanate to polyol (NCO/OH). All concentrations were percent by weight as used in the complete formulations. The ratio of isocyanate to polyol (NCO/OH) was obtained by dividing the isocyanate equivalents by the polyol equivalents. The interactions ( $X_1$ ,  $X_2$ , etc.) were calculated by simple multiplication of respective independent variables. Complete data or

variables and interactions as used in the analyses is presented in Table 9.

The data on coating properties and responses are presented in Table 10. Room temperature impact flexibility ( $Y_1$ , %) and glass transition temperature ( $Y_3$ , °C) values were used as obtained. However the data from low temperature flexibility and solvent resistances ( $Y_4$ ,  $Y_5$ , and  $Y_6$ ) were modified. For low temperature flexibility the following designations were used:

-1 if Panel fails on 1" mandrel  
0 if Panel passes on 1" mandrel  
1 if Panel passes on 1/2" mandrel  
2 if Panel passes on 3/8" mandrel

Solvent resistance data were measured in terms of pencil hardness. A negative sign indicates a decrease from the original hardness and the number reflects the decrease in pencil hardness units.

A stepwise regression analysis of the data (Tables 9 and 10) by the computer yielded the following correlation equations:

$$Y_1 = -38.4 + 5.7 X_3 + 0.16 X_2 X_3 + 1.26 X_2 X_4 - 1.3 X_3 X_4 \quad (1)$$

$$Y_2 = -0.81 + 0.93 X_1 X_3 \quad (2)$$

$$Y_3 = -81.4 + 2.43 X_2 + 1.24 X_3 + 45.6 X_4 - 2.48 X_1 X_4 \quad (3)$$

$$Y_4 = -4.97 + 1.98 X_4 \quad (4)$$

$$Y_5 = -2.6 + 1.14 X_4 \quad (5)$$

$$Y_6 = 0.65 + 0.14 X_3 - .35 X_1 X_3 + 1.6 X_1 X_4 - .13 X_2 X_3 - .015 X_2 X_4 \quad (6)$$

The equations (1) through (6) were then used to calculate compositions for desirable properties. Three sets of desired properties ( $Y_1$  to  $Y_6$ ) and the corresponding compositions ( $X_1$  to

TABLE 9

Data on Independent Variables and Interactions  
as used in Regression Analysis

$X_1$	$X_2$	$X_3$	$X_4$	$X_5$	$X_6$	$X_7$	$X_8$	$X_9$	$X_{10}$
Catalyst	[AU-568]	[PCP-0300]	NCO/OH	$X_1X_2$	$X_1X_3$	$X_1X_4$	$X_2X_3$	$X_2X_4$	$X_3X_4$
0.0	31.3	0.0	1.2	0.0	0.0	0.0	0.0	38.8	0.0
0.6	27.1	3.1	1.2	16.3	1.9	0.7	84.0	31.0	3.7
0.0	22.6	0.0	2.0	0.0	0.0	0.0	0.0	45.	0.0
0.6	21.5	2.4	1.9	12.9	1.4	1.4	51.6	40.9	4.6
0.6	17.8	5.9	1.8	10.7	3.5	1.0	105.0	31.5	10.4
0.5	14.9	5.0	1.8	7.5	2.5	0.9	74.5	26.4	8.8
1.1	5.6	17.9	1.3	6.2	19.7	1.4	100.2	7.3	23.3
1.1	4.5	19.5	1.3	4.9	21.5	1.4	87.8	5.7	24.8
1.1	2.4	21.4	1.2	2.6	23.5	1.4	51.4	3.0	26.5
1.1	1.8	15.7	2.1	2.0	17.3	2.3	28.3	3.7	32.0
1.1	0.0	17.4	2.0	0.0	19.1	2.2	0.0	0.0	0.0
1.1	0.0	24.0	1.3	0.0	26.4	1.4	0.0	0.0	30.0

**TABLE 10**  
**Response Data used in Regression Analysis**

$Y_1 =$ Room Temp. Impact (%)	$Y_2^1 =$ Low Temp. Flexibility	$Y_3 =$ Glass Transition Temp., ( $^{\circ}C$ )	$Y_4^2 =$ Lube oil Resistance	$Y_5^2 =$ Hydrocar- bon Resistance	$Y_6^2 =$ Skydrol Resistance
15	-1	51	-2	-1.0	0.0
20	-1	41	-1	-2.0	0.0
15	0	65	-2	0.0	1.0
30	-1	56	-2	0.0	0.0
40	0	49	-1	-0.5	0.0
30	-1	39	-2	-1.0	0.5
60	1	9	-3	-1.0	-3.0
60	1	8	-3	-1.0	-3.0
60	1	7	-3	-1.0	-3.0
15	1	31	0	-1.0	0.0
60	1	27	0	0.0	0.0
60	2	0	-3	-1.0	-3.0

1. -1: Fail 1" mandrel; 0: passes 1" mandrel; 1: Passes 1/2" mandrel and 2: Passes 3/8 mandrel.
2. A minus sign indicates a decrease in pencil hardness and the number denotes difference from the original.

X<sub>4</sub>) as predicted by equations (1) through (6) are presented in Table 11, columns (2) and (1) respectively. The column 3 of the same Table 11 also records the experimentally obtained properties for those specific compositions.

As shown in Table 11 a good correlation was obtained between desired and experimentally obtained glass transition temperatures (Y<sub>3</sub>). The solvent resistance properties (Y<sub>4</sub>, Y<sub>5</sub>, and Y<sub>6</sub>) in most cases were better than what was predicted. However the correlation between predicted impact and low temperature flexibilities and actually obtained values were not good. One of the possible reasons for lack of correlations was the exclusion of film thickness as one of the independent variables.

#### 6. Reactive Diluents

The use of reactive diluents as means of reducing solution viscosity while maintaining a high volume solids content was investigated. The reactive diluents selected from the product literature to be the most promising for this purpose were either solids or waxy solids. Dissolution of these materials was difficult, and at times impossible, due to the minimal amount of solvent which could be used. For this reason, this investigation was discontinued.

#### B. Cargill 5770 Evaluation

##### 1. Initial Evaluation

As part of the ongoing review of the commercial products literature, Cargill 5770, a polyester polyol from Cargill Inc.,

TABLE 11  
Correlation of Properties and Compositions\*

Desired Properties	Compositions (as calculated from Equations 1 through 6)	Formulation Numbers	Experimentally obtained Properties
$Y_1 = 43$	$X_1 = 0.56$	2442-193A	$Y_1 = 20$
$Y_2 = 0$	$X_2 = 12.3$		$Y_2 = -1$
$Y_3 = 46$	$X_3 = 10.4$		$Y_3 = 40$
$Y_4 = -1.0$	$X_4 = 1.8$		$Y_4 = -0.5$
$Y_5 = -0.5$			$Y_5 = -1.0$
$Y_6 = -0.3$			$Y_6 = 0.0$
$Y_1 = 65$	$X_1 = 0.54$	2442-193B	$Y_1 = 30$
$Y_2 = 0$	$X_2 = 14.5$		$Y_2 = -1$
$Y_3 = 27$	$X_3 = 12.7$		$Y_3 = 33$
$Y_4 = -2.3$	$X_4 = 1.3$		$Y_4 = -1.0$
$Y_5 = -1.1$			$Y_5 = -2.0$
$Y_6 = -1.5$			$Y_6 = 1.0$
$Y_1 = 56$	$X_1 = 0.54$	2442-193B	$Y_1 = 20$
$Y_2 = 0$	$X_2 = 13.5$		$Y_2 = -1$
$Y_3 = 32$	$X_3 = 11.7$		$Y_3 = 33$
$Y_4 = -2.0$	$X_4 = 1.5$		$Y_4 = -1.0$
$Y_5 = -0.9$			$Y_5 = -2.0$
$Y_6 = -1.0$			$Y_6 = -0.5$

\* See Table 9 and 10 for X and Y designations.

Chemical Products Division, was identified as a potential polyol candidate for incorporation into high solids systems. Using this polyol as the binder in the pigment blend and Desmodur N-100 as the crosslinking agent, formulations were prepared in which the pigment volume concentrations (PVC) and isocyanate (NCO/OH) levels were varied.

All of the formulations exhibited impact flexibility performances, both before and after heat aging, which met the program requirements. The low temperature flexibility performances needed further upgrading.

Overall, the Cargill 5770/Desmodur N-100 pigmented resin system exhibits good flexibility performances, but poor fluid resistance properties.

## 2. Blending Study

Analogous to the study in which the materials selected during the initial screening process were blended to optimize performance properties, a similar study blending the Cargill 5770 was carried out. The Acryloid AU-568 resin systems, form films which exhibit good fluid resistance but poor flexibility performances, the opposite trend of the Cargill 5770 systems. The two materials were blended together and crosslinked with either Desmodur N-100 or L-2291.

The formulations prepared incorporated the two hydroxy functional materials as major and minor polyol components within the pigmented portion of the two-package system. The minor polyol was defined as the material which replaced ten



and twenty-five weight percent of the other polyol. These blends were used to prepare pigment dispersions and then crosslinked with the designated polyisocyanate. This resulted in four major polyol/minor polyol/polyisocyanate resin combinations: Acryloid AU-568/Cargill 5770/Desmodur N-100, Acryloid AU-568/Cargill 5770/L-2291, Cargill 5770/Acryloid AU-568/Desmodur N-100, and Cargill 5770/Acryloid AU-568/L-2291. The PVC and NCO/OH levels were also varied.

Overall, the blended systems exhibited poor fluid resistance to hydrocarbon fluid. The systems incorporating Acryloid AU-568 as the major polyol also softened unacceptably upon immersion in Skydrol 500B fluid. Those systems incorporating Cargill 5770 as the major polyol, exhibited poor lubricating oil resistance.

The flexibility performances, with the exception of the low temperature performance, were acceptable for the Cargill 5770/Acryloid AU-568/Desmodur N-100 formulations.

As a result of this study, one formulation (2408-171) resulted. With the exception of room temperature impact, this topcoat system meets the chemical and physical requirements. (Tables 12 and 13).

Table 12

Formulation 2408-171 Composition

<u>Material</u>	<u>Weight Percent</u>	<u>Volume Percent</u>
TiO <sub>2</sub>	21.6	6.5
Acryloid AU-568	15.3	20.0
Cargill 5770	6.1	6.3
L-2291	35.3	36.4
Urethane Grade MEK	20.9	30.0
DBTDL (1% in MEK)	0.8	0.8

-----  
PVC = 10%

NCO/OH = 2.15

3. Continued Evaluation of Formulation 2408-171

Previous evaluation of the oxazolidine-polyol pigmented component of a two-package polyurethane system indicated a stability problem. It was assumed that a similar situation may be encountered with the Acryloid AU-568/Cargill 5770 component of formulation 2408-171. Therefore, long-term stability studies of the Acryloid AU-568/Cargill 5770/TiO<sub>2</sub> pigment grind were carried out.

a. Long Term Stability

The stability studies were conducted by monitoring the viscosities of the pigment grinds at periodic intervals: 24 hours, 1, 2, and 3 weeks. In one case, the grind was also evaluated immediately after being prepared. This was done to eval-

Table 13

Performance Properties of Formulation 2408-171

Composition	AU-568/Cargill 5770/Des N-100
Impact Flexibility	40% (60) <sup>a</sup>
High Temperature Stability- Impact Flexibility	60% (60) <sup>a</sup>
Low Temp. Flexibility- Straight Mandrel	25.4 mm (25.4 mm) <sup>a</sup>
60° Gloss	92 (90)
5% Salt Spray	No effect
100% Relative Humidity	No effect
Fluid Resistance <sup>b</sup>	
Initial Pencil Hardness	HB
Lubricating Oil (24 hours at 124°C)	0(1) <sup>a</sup>
Hydrocarbon Fluid (7 days at 25°C)	0(1) <sup>a</sup>
Hydraulic Fluid (7 days at 25°C)	0(1) <sup>a</sup>
Skydrol 500B (7 days at 25°C)	0(2) <sup>a</sup>
Distilled water (4 days at 38°C)	0(1) <sup>a</sup>

---

a. Program Goals

b. Indicated as a decrease in pencil hardness units following immersion.

uate the effect of moisture which may have been incorporated during the grinding process. At the time the viscosities were checked, film properties of the complete formulations were also determined.

The polyester polyol (Cargill 5770) is higher in acid number (10 vs. 0.03) than the polycaprolactone polyol (NIAX PCP-0300). Because the ring opening reaction of the oxazolidine oligomer is acid catalyzed, it was anticipated that pigment grinds containing Cargill 5770 would be more unstable compared to those containing NIAX PCP-0300.

The viscosity rise of the Cargill 5770 pigment grind was higher (33% vs 14%) than what was noted earlier with the pigment grinds containing the NIAX PCP-0300. In the absence of any chemical characterization data, it is difficult to predict what changes are occurring within the system causing the viscosity to increase. Also, it appears that if any moisture is incorporated into the grind during preparation, it does not adversely affect the pot-life.

With the exception of slightly decreased solvent resistance in Type III (hydrocarbon) fluid, major coating properties were unaffected by the room temperature aging of the pigment grind.

Analogous to the long term stability studies of the pigment grinds at room temperatures, the Acryloid AW-568/Cargill 5770/TiO<sub>2</sub> dispersion was also evaluated for the effect of aging at elevated temperatures. After aging 20 days at 53.9°C

(130°F), the Cargill 5770 grind exhibited more than a three-fold viscosity increase. The fully blended formulation (2408-171) incorporating the aged pigment grind, exhibited higher initial viscosity and shorter pot-life than formulations using the grinds aged at room temperature (Figure 13). The high temperature aging of the pigment grind did not significantly change the performance properties of the formed films.

Due to the lack of a usable pot-life and a sufficient shelf-life, further evaluation of formulation 2408-171 was not undertaken.

#### C. Evaluation of DeSoto Polyester Resin

As part of the ongoing review of available materials for incorporation into high solids systems, a polyester resin (2651A-93), manufactured by DeSoto, was investigated. Review of the patent literature<sup>3</sup> indicated that when formulated as a conventional topcoat (approximately 30 percent volume solids), over varying ranges of NCO/OH and PVC levels, the resulting formed films exhibit good performance properties. A series of nine formulations, varying from 1.5 to 2.5 NCO/OH and 10 to 25 percent PVC, and crosslinked with Desmodur N-100, were prepared and evaluated for performance properties.

From the data accumulated, it was noted that the formulations at 2.5 NCO/OH have acceptable resistance to softening in all test fluids. The formulations at lower NCO/OH levels are susceptible to excessive softening in Skydrol 500B and hydrocarbon fluids.

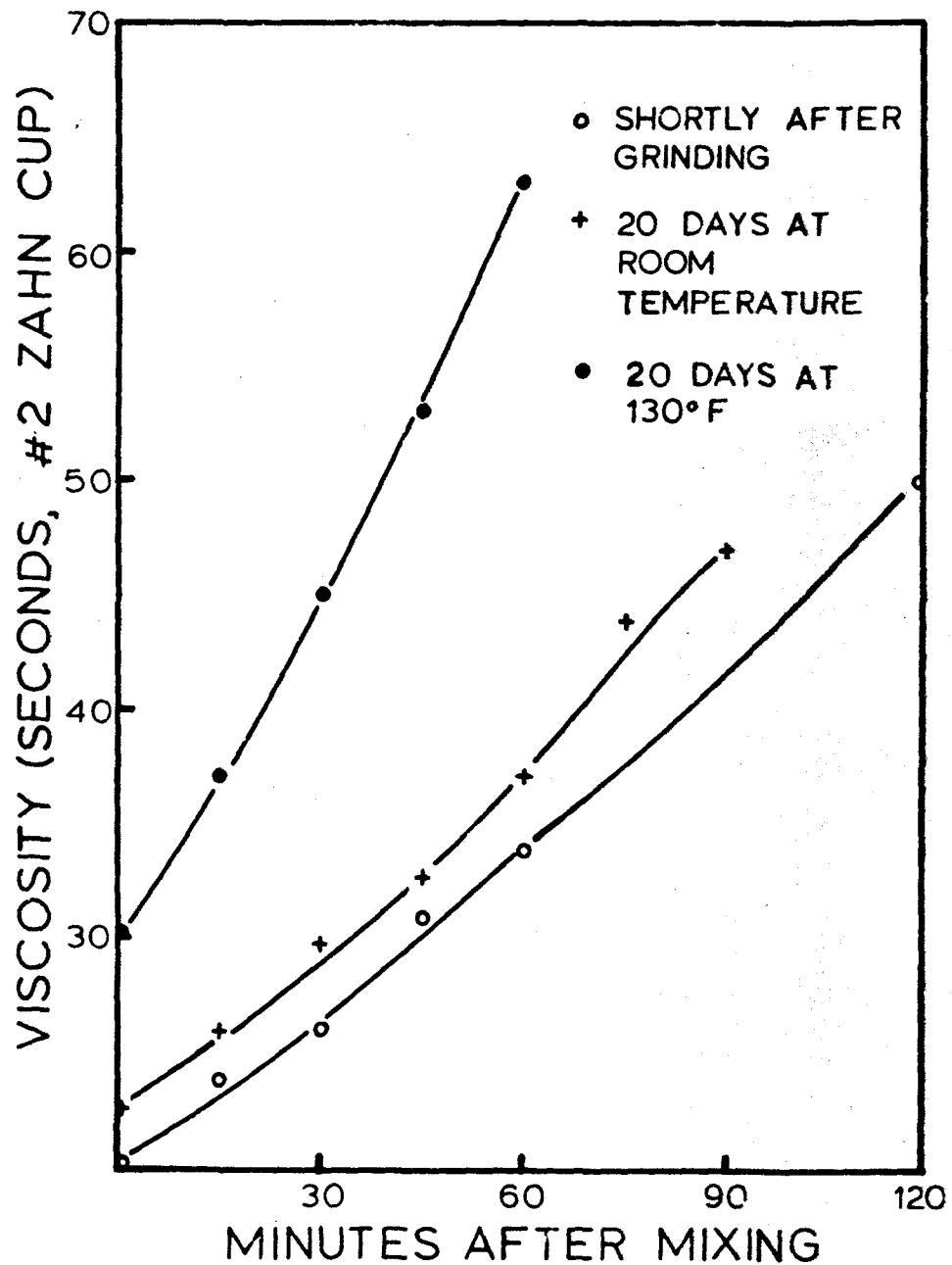


Figure 13: Effect of Accelerated Aging on Pot-life of Acryloid U-569/Cargill 5770/TiO<sub>2</sub> Grinds Mixed with Desmodur L-2291<sup>2</sup>

The performance properties exhibited were less than acceptable with respect to the program goals. However, two formulations, both at 10 percent PVC with NCO/OH levels of 1.5 and 2.5, exhibited borderline low temperature flexibility, one of the more difficult requirements to meet. (Borderline acceptability occurs when only one of the duplicate test panels passes).

During the evaluation of the test formulations, several areas of concern became apparent. The initial viscosities of the fully formulated systems were 2 to 3 times greater than allowed by the program requirements. The high viscosities resulted in coarse atomization and poor leveling properties, which could be improved, but not totally alleviated by increasing the air pressure of the spray system from 50 to 65 psi. The pot-life of the formulations were considerably shorter than the two hour minimum requirement. The formed films exhibited an orange peel texture, most probably a direct result of the insufficient leveling, as well as a considerable amount of foaming. Also, if the film thickness was excessive, sagging would occur.

To further evaluate the problems, the pot-life of formulation 2651A-44 (PVC = 10%, NCO/OH = 2.5, 65% volume solids, and reasonably good performance properties) was evaluated and found to be less than one hour.

To determine if the pot-life could be extended by reducing the volume solids content, formulation 2651A-44 was prepared at 65, 60, 55, and 50 percent volume solids levels. The pot-lives

of these formulations were determined (Figure 14). From the data, it appeared that an optimum formulation, with respect to pot-life, exists with a volume solids level between 60 and 55 percent. To pinpoint this optimum, formulations varying by one percent volume solids between these two levels were prepared and the pot-lives determined.

From the data presented in Figure 15 it is evident that the formulation at 56 percent volume solids exhibits an initial viscosity and pot-life within the program goals. However, this formulation exhibits an exponentially increasing viscosity while the formulation at 55 percent volume solids has a linearly increasing viscosity. Because of this fact and the relatively small difference in volume solids content, it would be advantageous to use the formulation having the lower volume solids level.

An alternative approach to lowering the initial viscosity of the 2651A-93/Desmodur N-100 high solids topcoat formulations was to heat the two components of the system and blend them together immediately before application with a heated spray gun. However, it was anticipated that heating the formulation would result in a faster cure rate and shorter pot-life. To investigate this, the two components of the topcoat formulation were heated to 53.9°C, blended together, and the pot-life determined. The temperature was maintained at 53.9°C. Although the initial viscosity was less than when at room temperature, the heated system gelled in less than 45 minutes.



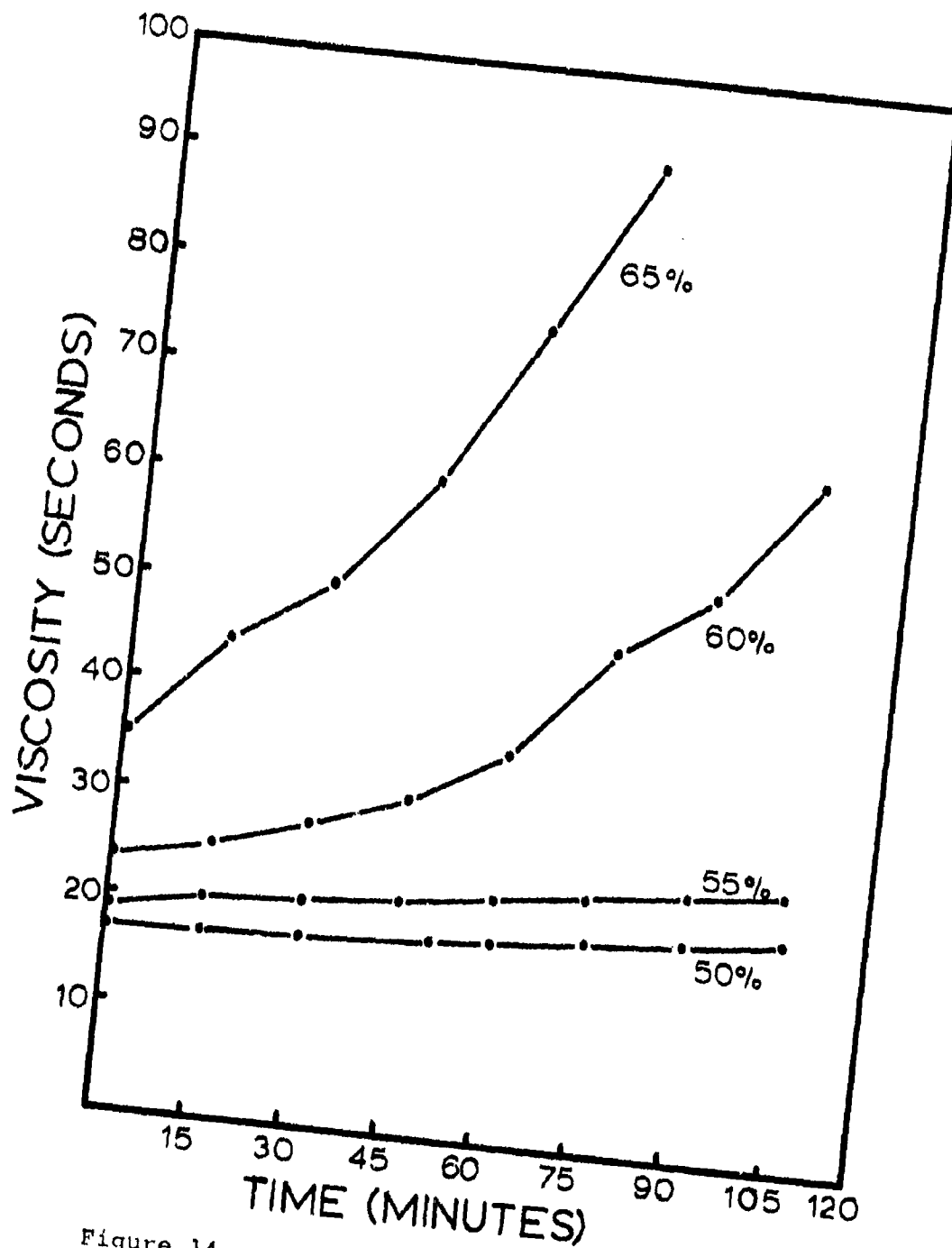


Figure 14: Pot-life vs. Percent Volume Solids  
(2651A-93 Polyester Resin)

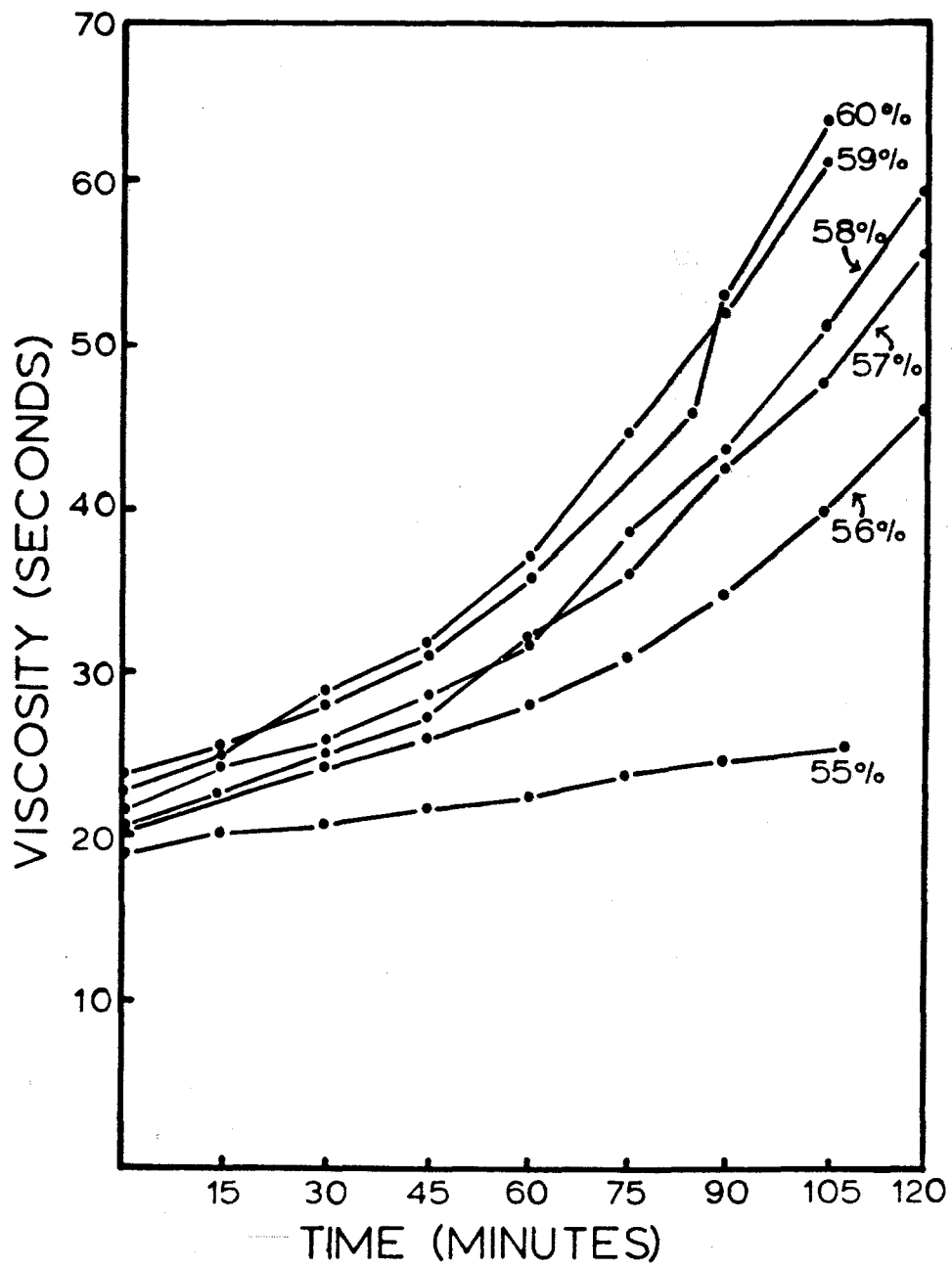


Figure 15: Determination of Optimum Volume Solids with Respect to Pot-life

Due to the problems of high initial viscosity, short pot-life, and generally unacceptable performance properties encountered further work with this resin system was not undertaken.

### III. Conclusions

1. The deficiencies in the Acryloid AU-568, NIAX PCP-0300 and Desmodur N-100 system make its use as a 65% volume solids high performance coating questionable. Further work needs to be done to find solutions to the problems encountered, (viscosity, stability, etc.). It may prove beneficial to synthesize a resin system, specifically designed for this end use, meeting the full range of performance properties.

2. The use of oxazolidine chemistry in high solids coating systems, as investigated during this program (i.e. formulations 2408-9 and 2408-171) does not appear practical. Significant difficulty rose in meeting the stability and pot-life requirements. Chemical modification may enable this resin to be suitable for this use.

3. In high solids coatings, the typical polyol-polyisocyanate prepolymer components cure too rapidly in high solids formulations. One effective method of slowing the reaction is to lower the volume solids content. Another is to lower the catalyst level within the formulation.

4. The use of additives (i.e. TEA and TEOS) aid in reducing the viscosity increases observed in the polyol component (a pigmented blend of oxazolidine and polyol) occurring during storage. However, the increases exhibited still result in a viscosity greater than the acceptable maximum.

5. The use of conventional air spray techniques for application of high solids coating systems is not practical. Control of the viscosity of the fully formulated system over a period of

two hours (the required pot-life) is a major concern. Use of a "Mix-in-Head" gun spray system may help to eliminate this problem.

#### IV. References

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3. F.A. Diaz and A.F. Leo, U.S. Patent 4,134,873 (DeSoto, Inc.), (1970).