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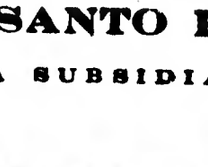

DAYTON LABORATORY

DAYTON, OHIO 45407

Quarterly Report No. 7
PHYSICAL AND RHEOLOGICAL PROPERTIES OF NITROSO RUBBERS

25 December 1964 through 24 March 1965

Contract No. DA19-129-AMC-151(N)
(O.I. 9115)

For

U. S. Army Natick Laboratories
Natick, Massachusetts

Authors

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ABSTRACT

Nitroso gums produced by Thiokol Chemical Corporation and supplied by the U.S. Army Natick Laboratories, Natick Massachusetts, were partially characterized. Linear expansion coefficients of a typical nitroso gum were determined to be 7.6×10^{-5} from -72°C up to the glass transition with the glass transition at -49°C. Density of the nitroso gum as received was 1.937±1 g/cc. A simple "finger printing" technique utilizing Vicat softening temperatures was devised. A typical Vicat temperature was -40°C. Volatile products representing up to 29 percent of the nitroso gum were collected. The products consisted of yet unidentified solvents and lower molecular weight portions. Atypicality (percent deviation from theoretical) was determined for the various gums. Atypicality varied from ±0.5% to ±4.0%. A change in typicality of the nitroso gum occurred with time and removal of the volatile product indicating loss of solvent and polymer constituent. Two $CF_3NO/C_2F_4/C_2F_3H$ terpolymers were examined.

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I. INTRODUCTION

The fluorinated nitroso rubber to be characterized in this program is considered to be a highly solvent-resistant, stable, low and high temperature rubber. The degree of its worth in these respects can only be determined through a characterization of its basic physical properties. The purpose of the characterization is to describe the rubber for its use and further improvement or modification.

Nine nitroso gum samples, listed as ZR-561-XP5675, XP5702, XP5812, XP5887, XP5807, XP5704, 0.2 C_2F_3H terpolymer, 0.5 C_2F_3H terpolymer, produced by the Thiokol Chemical Company, and a 3M produced gum were delivered to Monsanto Research Corporation via the Natick Laboratories for characterization.

Characterization consists of density, thermal expansion coefficients, infrared spectroscopy, nuclear magnetic (H^1 and F^{19}) resonance, elemental analysis, intrinsic viscosity, X-ray diffraction, differential thermal analysis, thermogravimetric analysis, Vicat softening temperature, Clash-Berg shear modulus, and typicality.

II. RESULTS

A. "APPARENT" LINEAR THERMAL EXPANSION COEFFICIENTS

Coefficients of linear thermal expansion by means of a dynamic modification of ASTM D696-44 were conducted on samples XP5675, XP5702, XP5812, and XP5887. A quartz dilatometer was used with specimens as designated in the ASTM specification. The dynamic modification consisted of periodic determinations of expansion as a function of temperature at a rate of about 1°C/minute. Standard procedure consists of end point determinations at an equilibrium temperature. The term "apparent" is used because of the non-equilibrium nature of these determinations. A temperature range from -75°C up to about 10C° above the glass transition temperature was covered.

Glass transition temperatures, Tg, where $\left(\frac{\partial \Delta \ell}{\partial T}\right) = 0$, were determined as a result of expansion measurements through and above that temperature.

The data is shown in Figures 1 through 4 and the coefficients and Tg's itemized in Table 1.

B. VICAT SOFTENING TEMPERATURES

A rapid method of fingerprinting gums for variations in initial physical properties has been desired. Toward this end, Vicat softening temperatures and curves were determined. The apparatus and procedure were according to ASTM D1525-58T. A temperature range from -75°C to above the softening temperature was covered.

Samples run were: XP 5675, XP5675 devolatized 16 hours @ 50°C and 3 mm Hg; XP5702, XP5702 devolatized 16 hours @ 50°C and 3 mm Hg; XP5812, XP5704, and the 0.5 molar ratio terpolymer. The Vicat softening data is shown in Figures 5 through 8 with Vicat temperatures in Table 2.

C. DENSITIES

Densities by liquid displacement were run on samples XP5675 and XP5702. They were:

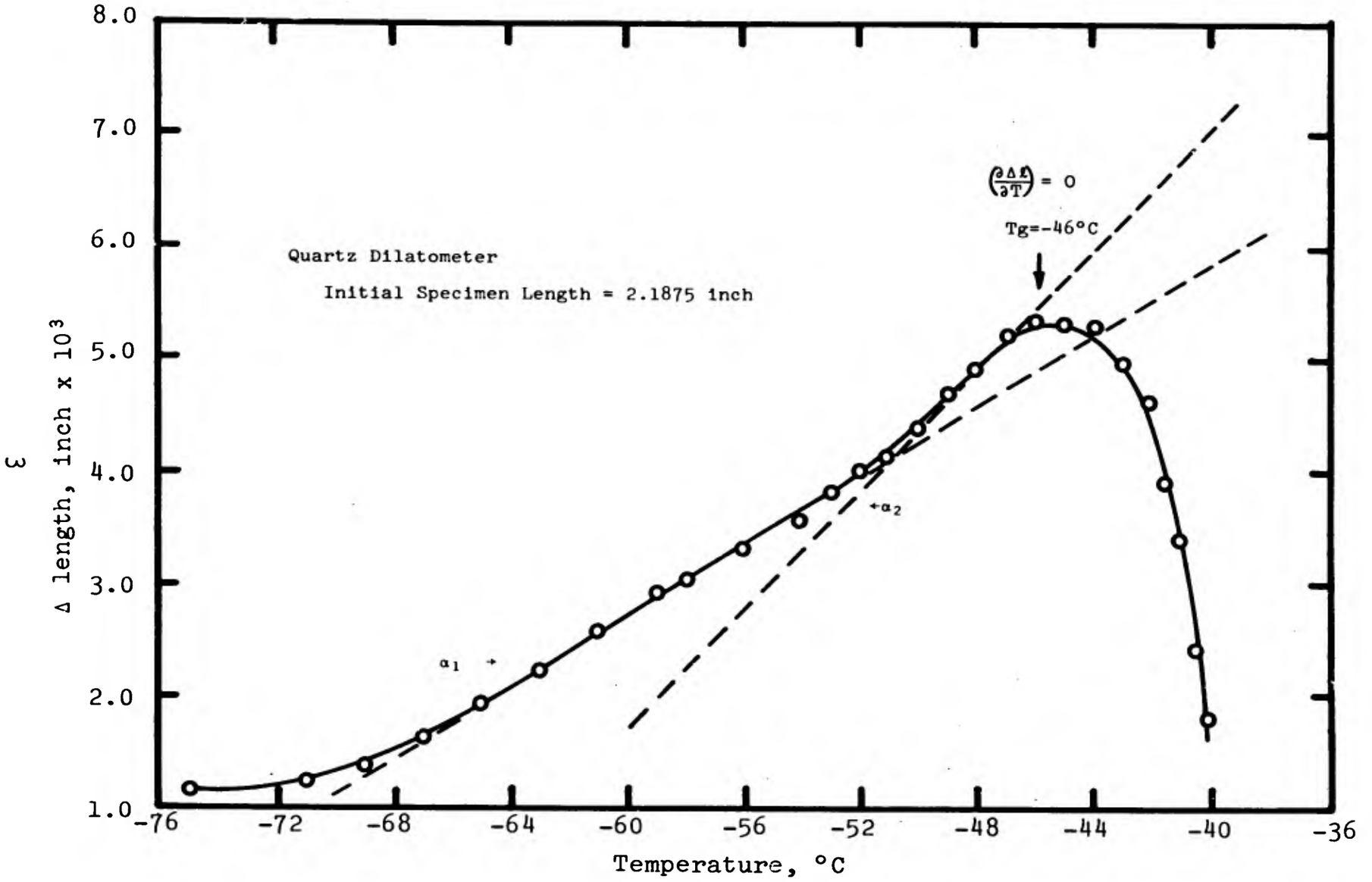


Figure 1. Thermal expansion of devolatilized XP5675 Nitroso Gum

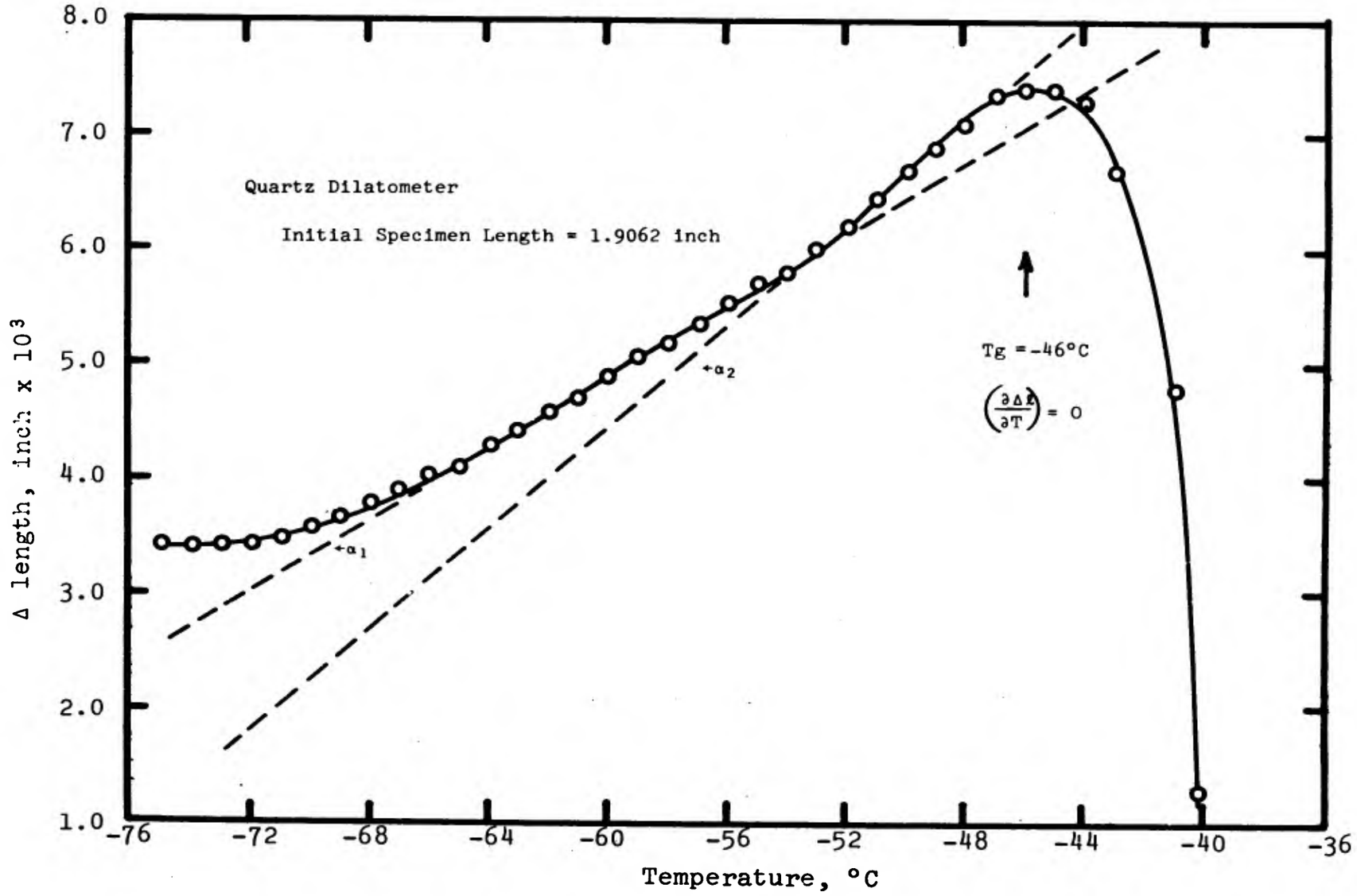


Figure 2. Thermal expansion of XP5702 Nitroso Gum

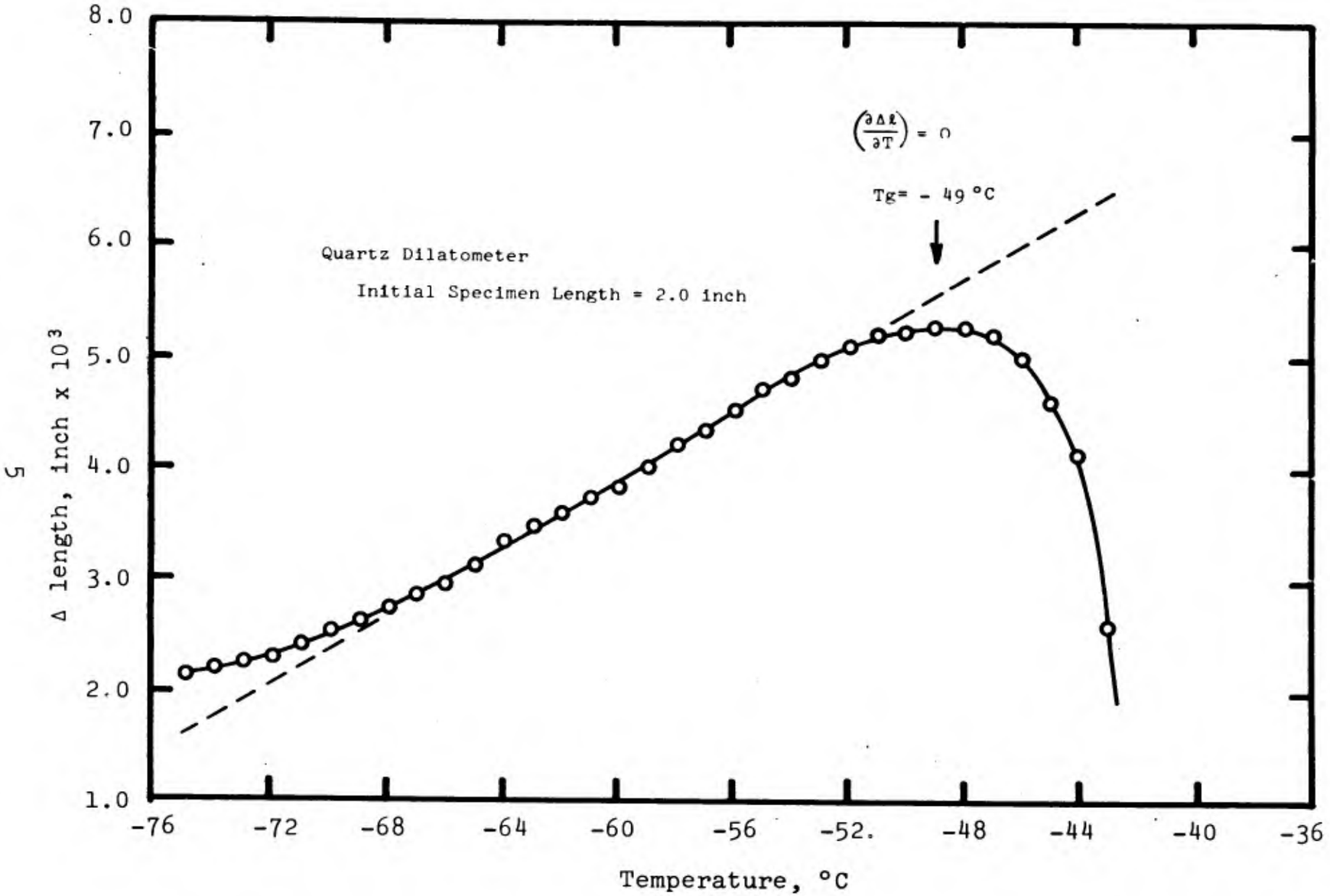


Figure 3. Thermal Expansion of XP5812 Nitroso Gum

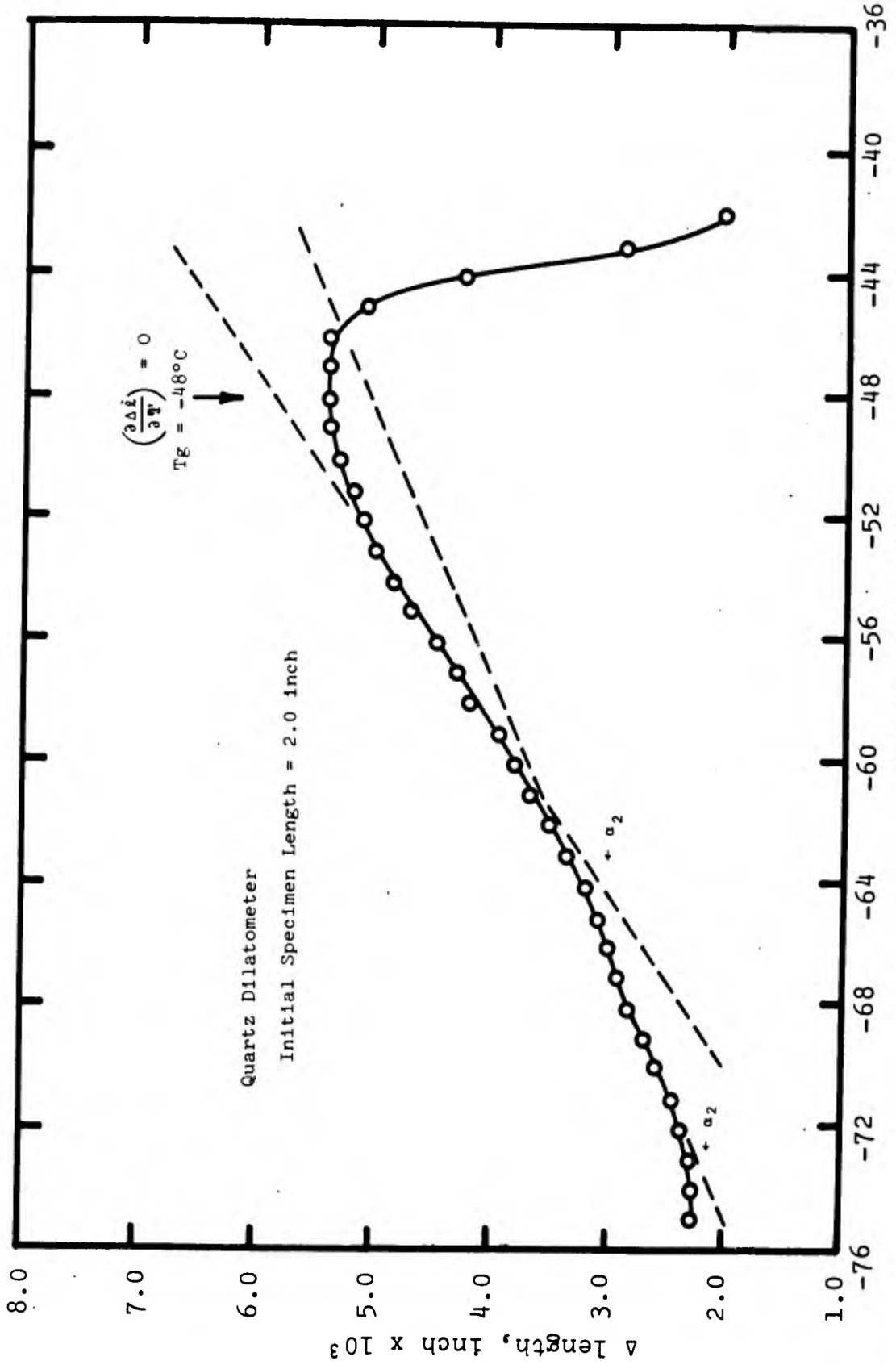


Figure 4. Thermal Expansion of Molded XP5887 Nitroso Gum

Table 1

"APPARENT" LINEAR THERMAL EXPANSION COEFFICIENTS OF ZR-561 NITROSO GUMS

Sample No.	"Apparent" Linear Expansion Coefficient,[a] °C^{-1}	Temperature Range, °C	Tg,[b] °C	Tg,[c] °C
XP5675[d]	7.2×10^{-5} 1.2×10^{-4}	-67 to -52 -52 to Tg	-46	-60[e]
XP5702	8.2×10^{-5} 1.2×10^{-4}	-67 to -52 -52 to Tg	-46	-45
XP5812	7.6×10^{-5}	-72 to Tg	-49	---
XP5887	5.7×10^{-5} 8.8×10^{-5}	-72 to -62 -62 to Tg	-48	---

[a] "Apparent" due to temperature rate rise of about 1°C/min. (See text).

[b] From thermal expansion data.

[c] From Clash-Berg determinations (see 6th Quarterly Report).

[d] Devolatilized 16 hours at 80°C and 3 mm Hg.

[e] On sample as received containing volatiles.

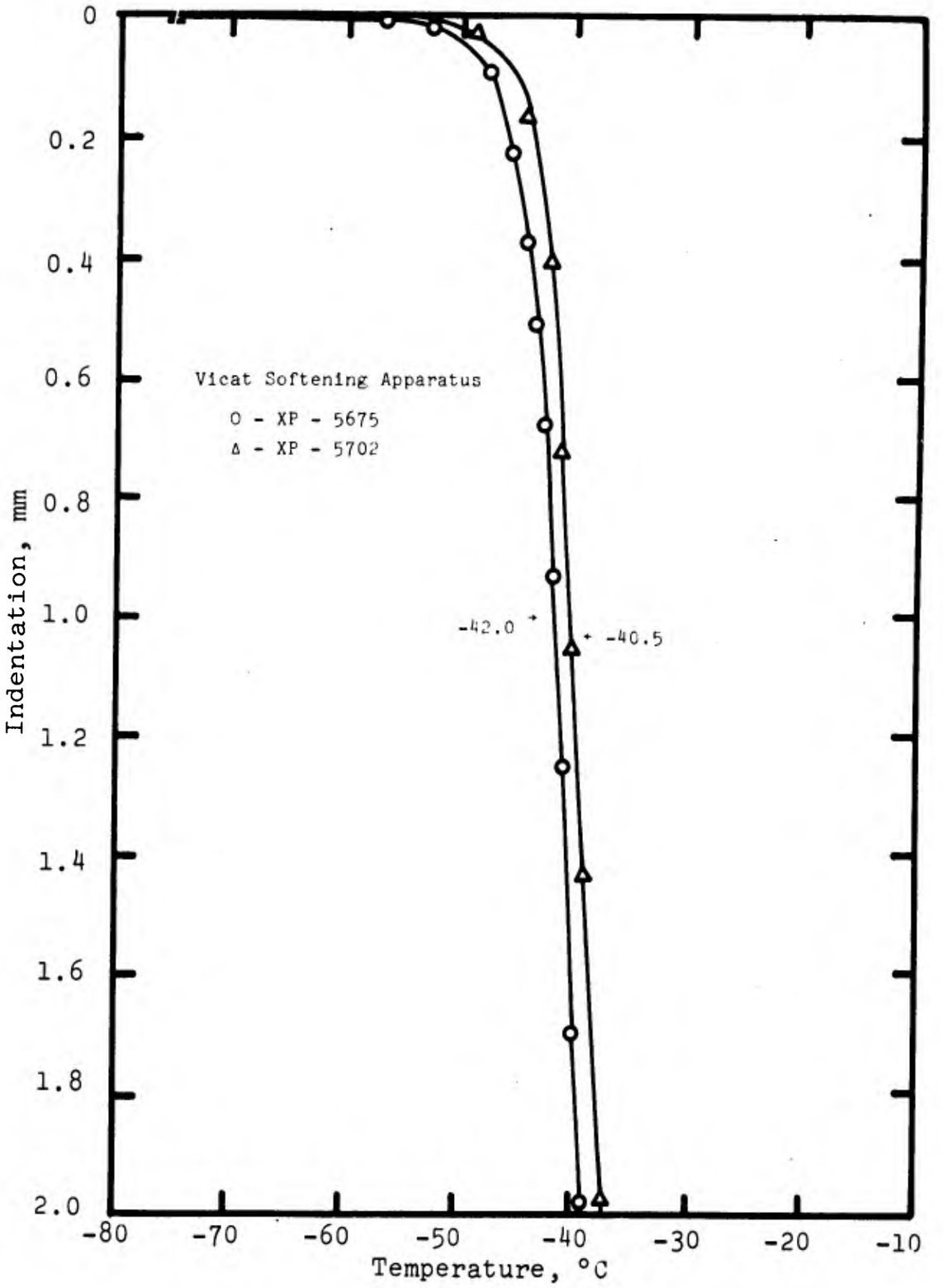


Figure 5. Vicat Softening Temperatures for XP5675 and XP5702 Nitroso gums as received

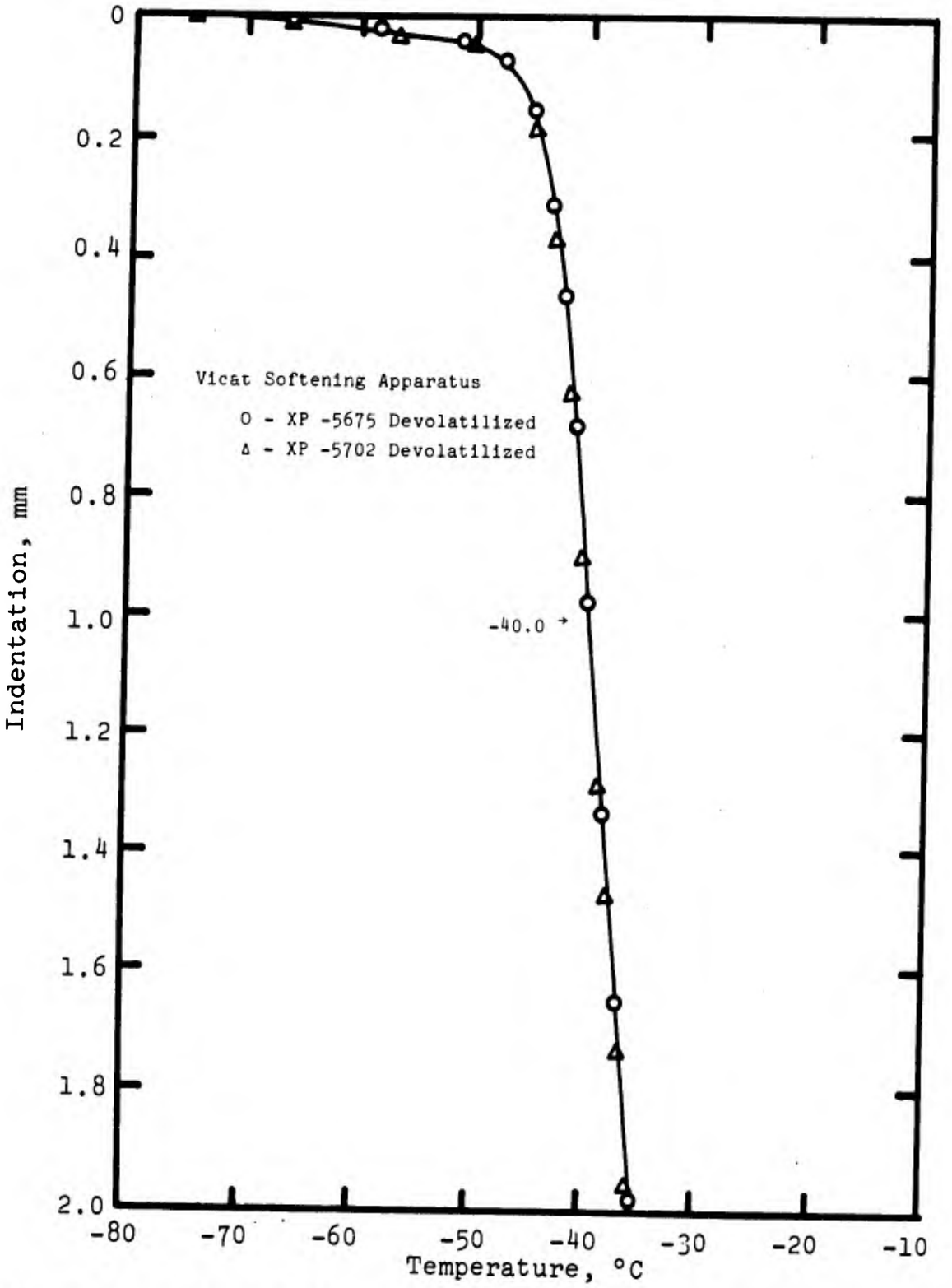


Figure 6. Vicat Softening Temperatures for Devolatilized XP5675 and XP5702 Nitroso gums

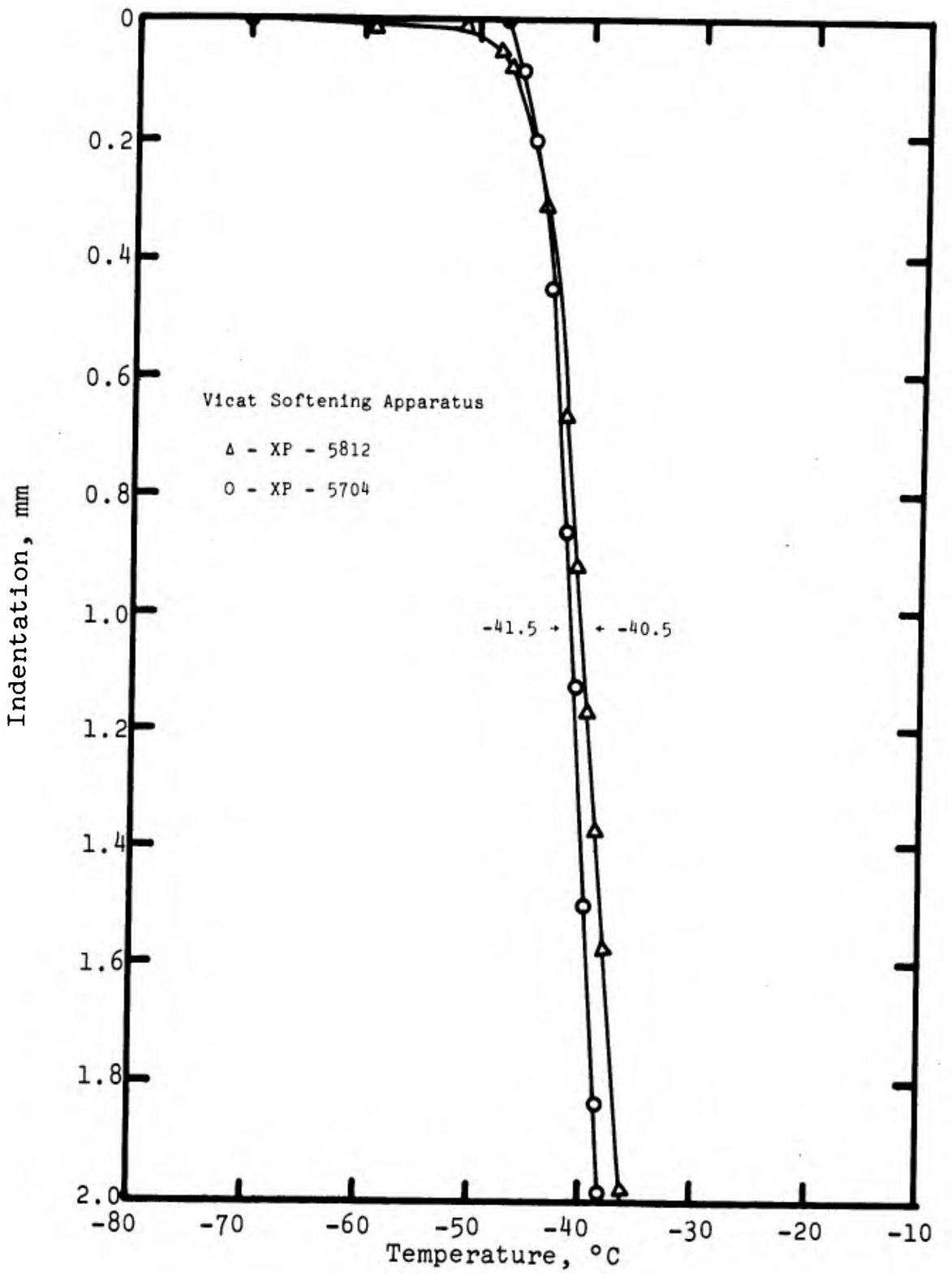


Figure 7. Vicat Softening Temperatures of XP5812 and XP5704 Nitroso gums as received

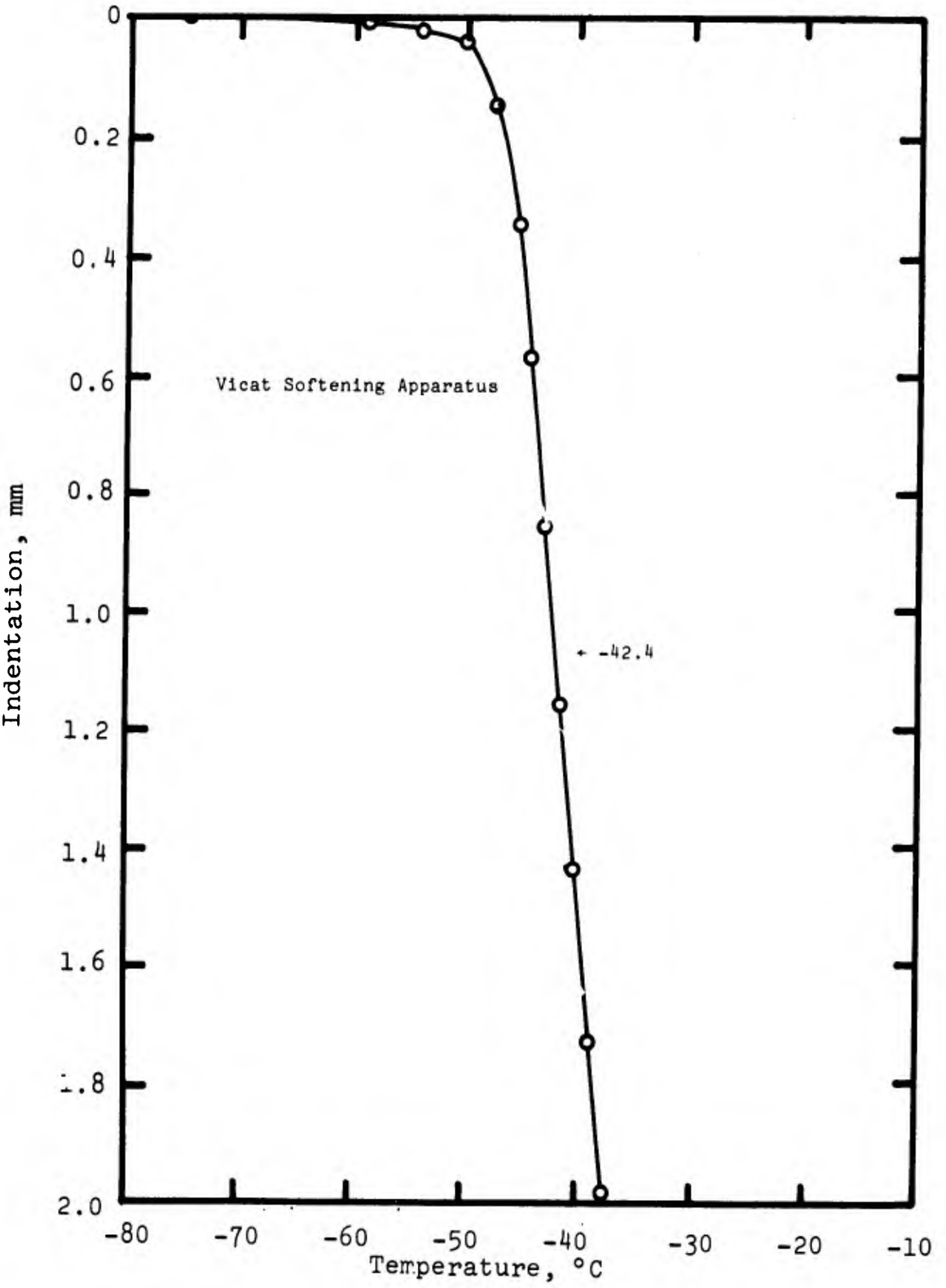


Figure 8. Vicat Softening Temperature of the 0.5 molar ratio terpolymer Nitroso gum

Table 2

VICAT SOFTENING TEMPERATURES
OF ZR-561 NITROSO GUMS

Sample No.	Softening Temp., °C[a]	Treatment
XP5675	-42.0	None, as received.
XP5675	-40.0	16 hrs. at 50°C and 3 mm Hg.
XP5702	-40.5	None, as received
XP5702	-40.0	16 hrs. at 50°C and 3 mm Hg.
XP5812	-40.5	None, as received
XP5704	-41.5	None, as received.
Terpolymer (0.5)	-42.4	None, as received.

[a] Temperature at 1 mm indentation; data should not be compared to other reported Vicat data as being significant.

Sample No.	Density	Treatment
XP	g/cc @ 25°C	
5675	1.936	None, As Received
5702	1.938	None, As Received

D. CHARACTERIZATION OF VOLATILES OF SAMPLE XP5675

Sample XP5675 exhibited a depressed glass transition temperature, as if plasticized, and gave indications of perhaps being contaminated with a volatile solvent or other similar material (Ref. 1). Isothermal TGA's were run at 125°C and 150°C to determine the weight loss due to volatilization. The TGA data is shown in Figure 9.

A third sample was run at 100°C and the volatiles trapped. A clear non-viscous liquid was recovered from the cold trap, and a viscous gum condensed in the delivery tube leading to the cold trap. The viscous gum was obviously low molecular weight nitroso gum. H^1 and F^{19} nuclear magnetic resonance results were obtained for the trapped, clear liquid. The proton resonance disclosed only a trace of water. The F^{19} resonance spectrum is shown in Figure 10. F^{19} resonance spectrum for Freon 113 and FC-75 are shown in Figures 11 and 12 for comparison.

E. ELEMENTAL ANALYSIS AND "ATYPICALITY"

In Table 3 is reproduced the elemental analyses data from Quarterly Report No. 6 (Ref. 1) with the addition of a column giving the weight percent standard deviation of the sample from theoretical. This quantity we have termed the "atypicality" of the sample and is:

$$\left(\frac{\Sigma(X-\overline{X})^2}{N-1}\right)^{1/2},$$

where X = analysis weight percent, $\overline{X}$ = theoretical weight percent, and N = number of elements reported. The closer the "atypicality" is to zero, the closer the sample is to theoretical.

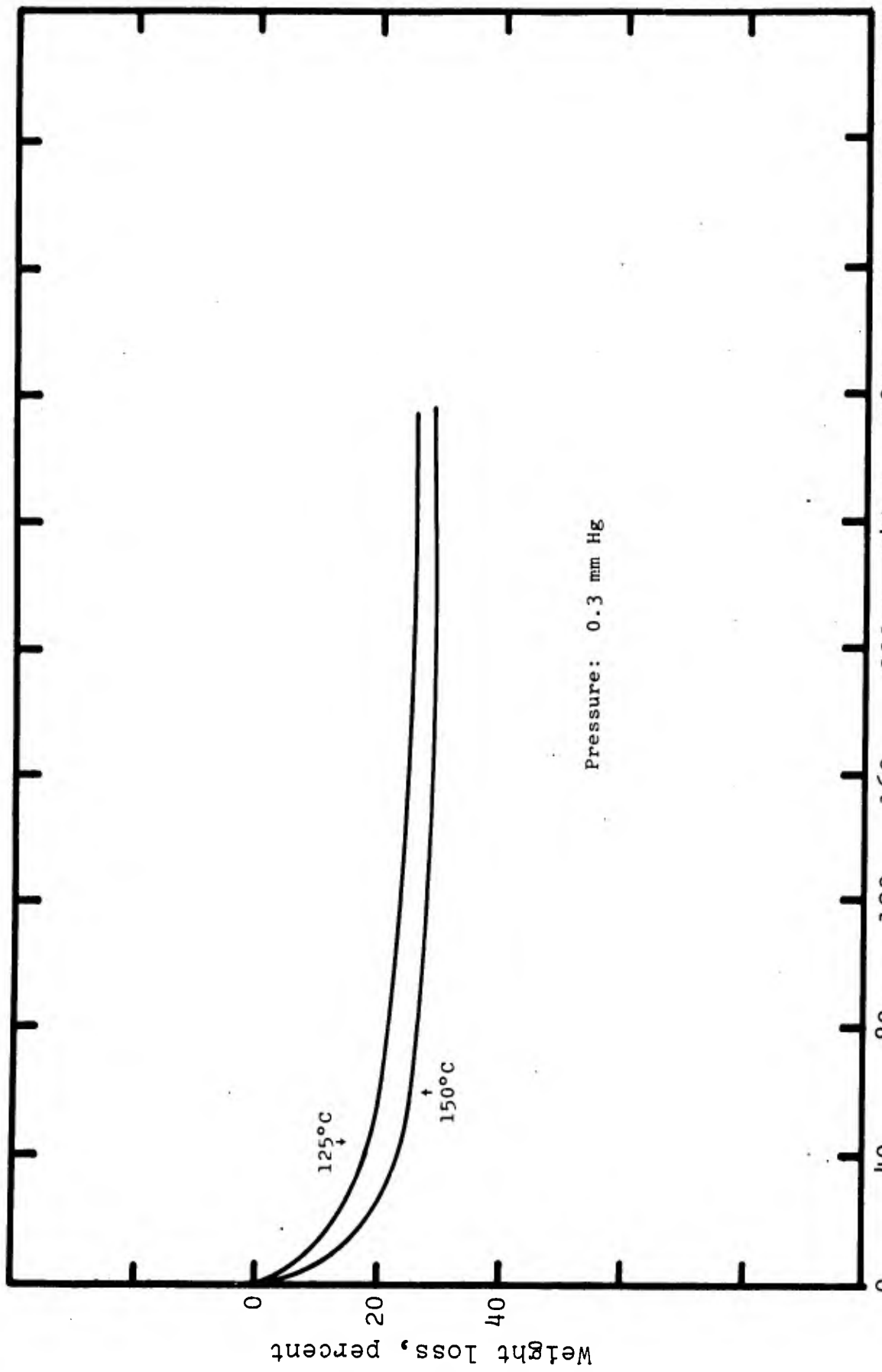
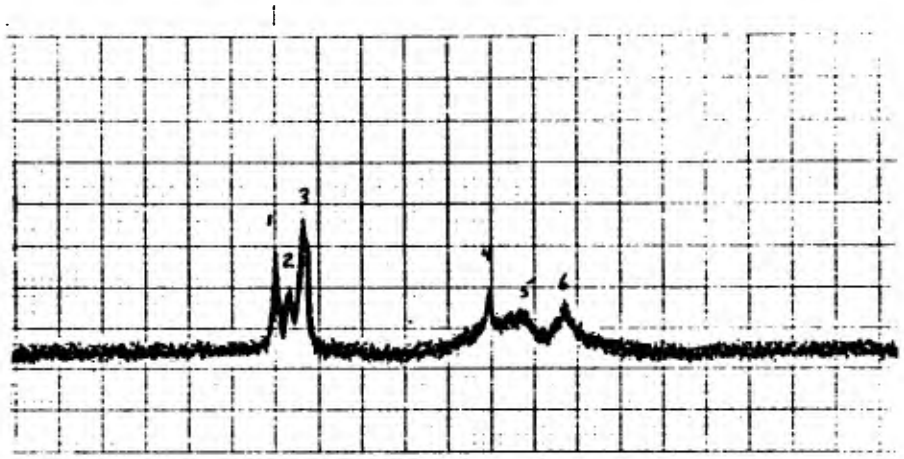


Figure 9. Isothermal Weight Loss at 125°C and 150°C for XP5675 Nitroso gum

RF Frequency: 40.0 Mc

Nuclei: F^{19}

Reference: Trifluoro acetic acid



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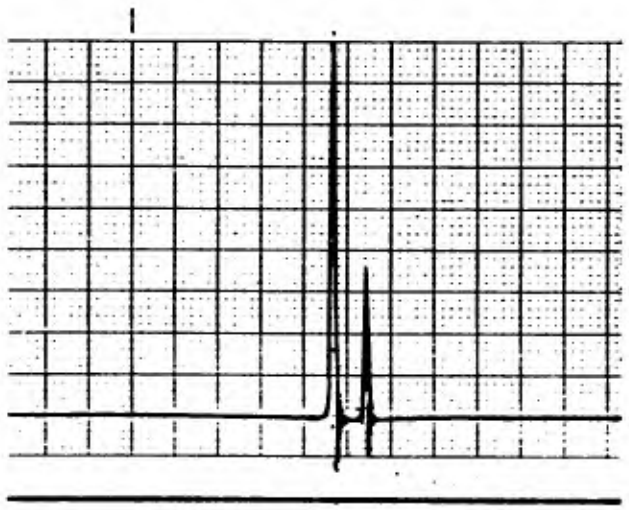
Peak	1	2	3	4	5	6			
PPM	-15.5	-14.0	-12.0	+9.0	+13.0	+18.0			
Area Ratio									

Figure 10. F^{19} NMR spectrum of clear volatile liquid from sample XP5675 gum

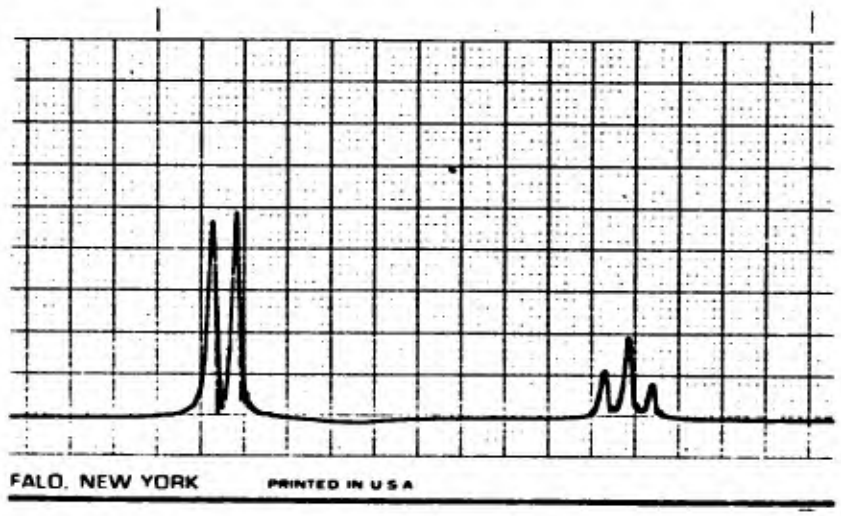
RF Frequency: 40.0 Mc

Nuclei: F^{19}

Reference: Trifluoro acetic acid



Freon
113



Peak	1	2				Slow Sweep			
PPM	-10.0	-6.0							
Area Ratio									

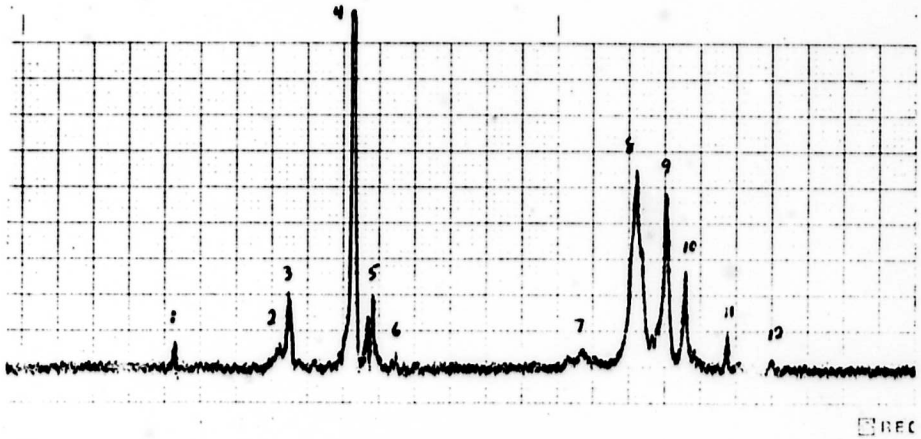
Figure 11. F^{19} NMR spectrum of Freon 113

RF Frequency: 40.0 Mc

Nuclei: F^{19}

Reference: Trifluoro acetic acid

FC-75



Peak	1	2	3	4	5	6	7	8	9	10	11	12
PPM	-20.5	-5.6	-4.4	+4.8	+7.4	+10.8	+37.4	+45.0	+49.4	+52.0	+58.0	+64.5
Area Ratio												

Figure 12. F^{19} NMR spectrum of FC-75

F. "ATYPICALITY" AND CONDITIONING (AGING) OF XP5675 NITROSO GUM

Elemental analyses of XP5675 nitroso gum was conducted in December 1964, again in March 1965, and after devolatizing in March 1965 for 16 hours at 80°C and 3 mm Hg. The analysis and "Atypicality" of these samples are shown in Table 4.

G. ANALYSIS OF NITROSO TERPOLYMER

Two terpolymers of $CF_3NO/CF_2CF_2/CF_2CFH$ containing respective molar ratios of 5/4.8/0.2 and 5/4.5/0.5 were examined by NMR (H^1 and F^{19}) and infrared. 9% solutions in Freon 113 and high concentrations of an evaporated solution were used as samples. The spectra were identical to those of the homopolymer with no proton resonance signal observed.

H. REFERENCES

1. "Physical and Rheological Properties of Nitroso Rubbers," Quarterly Report No. 6, Contract No. DA19-129-AMC-151(N) (O.I. 9115), 14 January 1965.

2. Shultz, A. R., N. Knoll, and G. A. Morneau, J. Polymer Sci., 62, 211 (1962).

Table 3

ELEMENTAL ANALYSIS AND "ATYPICALITY" OF ZR-561 NITROSO GUMS

Sample No.	C Wt. %	H Wt. %	N Wt. %	F Wt. %	O[a] Wt. %	Atypicality,[b] ± Wt. %
C_3F_7NO	18.10	0.00	7.04	66.82	8.04	0.00
XP5675	18.29±.12[c]	0.15 ±.07	6.27 ±.18	61.51 ±.16	13.79	3.94
XP5702	18.29±.06	0.12 ±.04	6.26 ±.05	66.06 ±.13	9.31	0.84
XP5812	18.54±.16	0.09 ±.03	6.30 ±.06	66.61 ±.15	8.46	0.49
XP5887	18.54±.04	0.06 ±.01	6.38 ±.00	67.34 ±.15	7.68	0.51

[a] Oxygen by difference.

[b] $\left(\frac{\Sigma(X-\overline{X})^2}{N-1}\right)^{1/2}$, where X = analysis, $\overline{X}$ = theory, N = no. of elements reported.

[c] Standard deviation of repeat analyses.

Table 4

ELEMENTAL ANALYSIS AND ATYPICALITY OF XP5675 NITROSO GUM WITH TIME

Analysis Date	C Wt. %	H Wt. %	N Wt. %	F Wt. %	O[a] Wt. %	Atypicality,[b] ± Wt. %
C_3F_7NO	18.10	0.00	7.04	66.82	8.04	0.00
12/10/64	18.29	0.15	6.26	61.51	13.79	3.94
3/ 6/65	18.52	0.00	6.75	58.54	16.19	5.82
3/ 6/65[c]	18.23	0.00	7.06	56.64	18.07	7.15

[a] Oxygen by difference.

[b] See Table 3 for definition.

[c] After devolatilizing for 16 hours at 80°C and 3 mm Hg.

III. CONCLUSIONS AND SUMMARY

Apparent linear expansion coefficients were measured on the various gums with the most typical gum (theoretically) exhibiting a value of $7.6 \times 10^{-5} °C^{-1}$ from -72°C up to the glass transition temperature. The less typical gums exhibited a change in their expansion coefficients between -72°C and their glass transition temperature.

The glass transition temperature (expansion coefficient method) for the most typical nitroso gum was -49°C. Other gums varied from -46 to -48°C (after devolatilization).

A rapid technique for "finger printing" to readily determine differences in batches and samples by variations in physical properties was devised using Vicat softening temperatures. Vicat temperature differences of ±0.25°C were shown to be significant. Removal of volatiles and impurities were noted by this technique. Determinations on a rough gum specimen as received could be completed in a period of less than two hours. This technique may not prove conclusive identity but will indicate differences. Relationship to glass transitions should be forthcoming.

Densities of the nitroso gum as received were shown to be 1.937±1 g/cc. This density includes volatile products.

Collection and analysis of the volatile products in the nitroso gum indicated a substantial low molecular weight portion and a clear liquid. These volatile products represented up to 29% of the weight of the sample. The clear liquid consisted of a yet unidentified solvent and a poorly identified nitroso gum component.

The "Typicality" or nearness of composition to theoretical was determined for the four samples XP5675, XP5702, XP5812, and XP5887. XP5812 and XP5887 were found to be typical within ±0.5% by weight of theoretical. Sample XP5675 deviated by almost ±4.0 percent. We would judge XP5812 and XP5887 as being most typical of a theoretical nitroso gum, however, not necessarily most typical of the manufactured Thiokol product.

A definite change in typicality with time and removal of volatile product was demonstrated. The typicality, however, decreased both with time and removal of the volatile. The significance of the typicality analysis is that (1) if the solvent alone were volatilizing away, the atypicality would decrease as the atypical contaminant was removed; (2) if monomer is volatized due to either depolymerization or incomplete conversion, the material either remains unchanged or increases in atypicality depending on whether or not co-monomers are

lost at the same rate. In as much as the atypicality increased on the nitroso sample, both on standing and upon devolatilization, we conclude that whether or not solvent is also being lost, a more important change seems to be the loss of a polymer constituent possibly through spontaneous depolymerization or some elimination reaction. Shultz, Knoll and Morneau (Ref. 2) described the degradation of nitroso gums by heat and radiation.

H^1 and F^{19} nuclear magnetic resonance indicated no difference between the $CF_3NO/CF_2CF_2/CF_2CFH$ terpolymer and the homopolymer. Sensitivities for the hydrogen will have to be improved.

IV. FUTURE PLANS

Further analysis of the 30 percent volatile product will be conducted to determine its characteristics, structure and source. Cleaning up of the various samples as received will be conducted, their typicality determined, and further characterization conducted. A comparison to the 3M gum will be made.

Molecular weight distribution and average molecular weight with light scattering analysis on gum fractions will be conducted. Various solvents will be treated for intrinsic viscosity versus molecular weight.

Analysis of the terpolymers will continue.

V. TIME AND FINANCIAL STATUS

	Hours (to 3/31)
George L. Ball III, Research Specialist*	628
Ival O. Salyer, Research Manager, Polymer Applications	74
Harry S. Wilson, Research Group Leader	278
John V. Pustinger, Analytical Group Leader	14
Lucius Gilman, Manager, Plastics and Polymer Research	130
William R. Smith, Analytical Chemist	5
Professional, Mixed	5
Professional	1134
Charlotte S. Fritsch, Research Technician	347
John E. Strobel, Research Tecnnician	37
Richard L. Evers, Research Technician	24
Margaret S. Ross, Research Technician	90
Gary A. Clinehens, Research Technician	46
Rodrigue G. Thibodeau, Research Technician	238
Conrad A. Cenerizio, Research Technician	26
Technical, Mixed	39
Technical	847
Grand Total	1981

* Project Leader

$26,138 has been spent as of 31 March 1965. The contract, less fee, is for $59,335, leaving a balance of $33,197.00.

46% of work has been completed and 44.1% of the money spent. The money remaining on the contract is sufficient. However, a 12-month extension in time will be necessary to complete the work.

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Dayton Laboratory
Dayton, Ohio 45407

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c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

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	Materials Research Branch Clothing & Organic Materials Division U.S. Army Natick Labs, Natick, Mass.

13. ABSTRACT

Nitroso gums produced by Thiokol Chemical Corporation and supplied by the U.S. Army Natick Laboratories, Natick, Massachusetts, were partially characterized. Linear expansion coefficients of a typical nitroso gum were determined to be 7.6×10^{-5} from -72°C up to the glass transition with the glass transition at -49°C. Density of the nitroso gum as received was 1.937 ± 1 g/cc. A simple "finger printing" technique utilizing Vicat softening temperatures was devised. A typical Vicat temperature was -40°C. Volatile products representing up to 29 percent of the nitroso gum were collected. The products consisted of yet unidentified solvents and lower molecular weight portions. Atypicality (percent deviation from theoretical) was determined for the various gums. Atypicality varied from $\pm 0.5\%$ to $\pm 4.0\%$. A change in typicality of the nitroso gum occurred with time and removal of the volatile product indicating loss of solvent and polymer constituent. Two $CF_3NO/C_2F_4/C_2F_3H$ terpolymers were examined.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Physical properties	8					
Rheology	8					
Nitroso rubber	9					

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13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U).*

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Idenfiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.