

Rheological Properties of Molten Poly(ethylene Terephthalate)

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Synopsis

The complete steady-state flow properties of molten poly(ethylene terephthalate) for shear stresses $\leq 4.14 \times 10^6$ dynes/cm² were determined. A single, complete master curve had been constructed in earlier work by Gregory and Watson; the curve interrelates the shear stress, shear rate, temperature, and molecular weight (inherent viscosity) by using a temperature superposition scheme from the literature and a similar molecular weight superposition scheme.

Equations in agreement with theory and with other published experimental data were derived from the master curve. Results presented here make possible the direct calculation of the melt viscosity of poly(ethylene terephthalate) at shear stresses $\leq 4.14 \times 10^6$ dynes/cm². The effects of a unit temperature change and/or a unit change in inherent viscosity (*I.V.*) on the melt viscosity were determined. For poly(ethylene terephthalate) with a 0.6 *I.V.*, a 0.0025 change in *I.V.* accounts for about the same change in melt viscosity as a 1°C change in temperature.

INTRODUCTION

The steady-state flow properties of poly(ethylene terephthalate) (PET) were reported earlier in graphic form by Gregory and Watson.¹ A single, complete master flow curve (one form of the rheological equation of state) was constructed in that work¹; the curve interrelated shear stress, shear rate, temperature, and molecular weight (as measured by inherent viscosity) by using a temperature superposition scheme from the literature²⁻⁴ and a similar molecular weight superposition scheme. The reader is referred to the earlier work¹ for the detailed development of the master curve. Briefly, however, flow curves were plotted for PET in terms of log shear stress at the wall, τ_w , versus log shear rate at the wall, $\dot{\gamma}_w$, over a range of temperatures (265° to 295°C), molecular weights (about 23,000 to 70,000), and shear rates (50 to 24,000 sec⁻¹). Mendelson's shear rate-temperature superposition scheme²⁻⁴ and an additional shifting to a single reference molecular weight were used to shift all data to a single master curve.¹

Since the earlier presentation of the master curve in graphic form,¹ rheological equations in agreement with theory^{5,6} and with other experimental data⁷⁻¹⁰ have been derived from the master curve. The objective of this paper is to present these equations as an extension of the earlier work. Re-

sults presented here now make possible the direct calculation of the melt viscosity of PET at shear stresses $\leq 4.14 \times 10^6$ dynes/cm².

EXPERIMENTAL

An Instron capillary rheometer was used to obtain the rheological data for molten PET. It is an extrusion-type instrument with a motor-drive piston, which induces a constant extrusion velocity to the fluid.¹¹ Three capillaries were used; the length/diameter ratios of the three were 10, 40, and 67.5. The polymer used was PET made by solid-phase polymerization.^{12,13} The inherent viscosities of the polymer samples, determined from the solution viscometry of 0.25 g polyester in 100 ml of a 60/40 mixture of phenol/tetrachloroethane, ranged from 0.35 to 0.82 and corresponded to a weight-average molecular weight range of about 23,000 to 70,000. Data for the calculation of τ_w and $\dot{\gamma}_w$ at temperatures of 265°C, 280°C, and 295°C for the shear rate range of 50 to 24,000 sec⁻¹ were obtained.

RESULTS AND DISCUSSION

Double superposition of all experimental data for all temperatures and all molecular weights investigated was achieved and is shown in the earlier publication.¹ Data points generally fall on the same smooth curve of $\log \tau_w$ versus $\log a_T B_{[M_w]} \dot{\gamma}_w$ (modified shear rate), where a_T is the temperature shift factor and $B_{[M_w]}$ is the weight-average molecular weight shift factor.

Temperature Shift Factor

The term a_T is the Mendelson²⁻⁴ temperature shift factor calculated at constant shear stress as the ratio of the shear rate for the reference flow curve to the shear rate for each of the other flow curves (for constant $I.V.$ with temperature the parameter).¹ The log of a_T is a linear function of the reciprocal absolute temperature.¹ A simple Arrhenius-type equation fit the data well:

$$\ln a_T = -11.9755 + \frac{6802.1}{T} \quad (1)$$

This relationship held for all molecular weight levels investigated.

Activation Energy for Flow

Activation energies, E_a , have been determined for the flow of several molten polymers,^{2-4, 14-16} including PET.^{7,17,18} Values reported for molten high-density polyethylene were 6 kcal/mole,¹⁶ 7 kcal/mole,¹⁴ and 6.3 kcal/mole,² and the values reported for low-density polyethylene were 13 kcal/mole,¹⁶ 11.3 kcal/mole,⁸ and 11 kcal/mole.⁴ Van der Vegt determined E_a for polypropylene to be 11 kcal/mole,¹⁶ and Mendelson reported 10 kcal/mole.⁴ Activation energies for molten polystyrene were reported as 35 kcal/mole¹⁶ and 28 kcal/mole.¹⁹ Reasonable agreement exists among the various sources.

Considerable disagreement exists in the reported values of E_a for molten PET, however. The earliest work found in the literature was by Marshall and Todd.¹⁸ They reported values of 40 kcal/mole for dried PET and 19 kcal/mole for undried PET and attributed the difference to a reduction in molecular weight caused by hydrolysis. Their analysis was based on experimental results obtained at three temperature levels. Considerable scatter existed in their $\log \eta_0$ (zero shear viscosity)-versus- $1/T$ data for dried PET. If one data point is ignored (high temperature of 335°C), however, E_a for the dried polymer is also approximately 19 kcal/mole (more in line with their data for undried PET and with most other data found in the literature). Aizenshtein and Petukhov¹⁷ measured melt viscosities of PET using a falling-ball viscometer (a questionable viscometer for melts). They determined E_a to be about 30 kcal/mole. Considerable scatter existed in their data, and for high molecular weight samples ($I.V.$ of about 0.7) at low temperature, the ball would not fall. Their results are thus open to serious doubt. Manaresi et al.⁷ determined E_a for PET to be a slight function of molecular weight and to average 17.2 kcal/mole. Martin and Kibler⁹ reported an E_a for PET of 0.63 $I.V.$ to be 18.6 kcal/mole from the data of Schulken.¹⁰ Schulken¹⁰ also determined a value of 13.6 kcal/mole for PET of low molecular weight.

The activation energy for flow determined in this investigation was 13.5 kcal/mole, and within experimental error it was independent of molecular weight in the 0.35 to 0.82 $I.V.$ range. This value agrees reasonably well with the work of Schulken¹⁰ and Manaresi et al.⁷ but not with that of Marshall and Todd¹⁸ and Aizenshtein and Petukhov,¹⁷ as explained previously.

Molecular Weight Shift Factor

The term $B_{[\bar{M}_w]}$ is the molecular weight shift factor calculated at constant shear stress as the ratio of the shear rate for the reference master curve (with temperature superposition) to the shear rate for each of the other master flow curves (with temperature superposition). The \log of $B_{[\bar{M}_w]}$ for PET is a linear function of the \log of the molecular weight.¹ The form of this relationship is similar to the Fox-Flory equation relating zero shear rate viscosity to molecular weight.⁶ The slope of the experimental $\log B_{[\bar{M}_w]}$ relationship is 3.5, which agrees well with the value of 3.5 ± 0.1 for the exponent in the Fox-Flory⁶ and Bueche⁵ equations. The equation relating the molecular weight shift factor to molecular weight is

$$B_{[\bar{M}_w]} = 1.49 \times 10^{-15} (\bar{M}_w)^{3.5}. \quad (2)$$

Development of Rheological Equations

The experimental rheological equation of state developed in earlier work¹ can be well represented by straight lines in the shear stress regions of 0 to 9.65×10^5 dynes/cm² and 9.65×10^5 to 4.14×10^6 dynes/cm². Data are sufficiently scattered for shear stresses greater than 4.14×10^6 dynes/cm² so that the true shape of the relationship between shear stress and modified

shear rate is not known; thus, no attempt was made to fit these data. A modified Bueche-Harding equation⁵ (to be published at a later date) was used to calculate the rheological equation of state in the shear stress region above 4.14×10^6 dynes/cm².

Lower Shear Stress Region ($\tau_w \leq 9.65 \times 10^5$ dynes/cm²). The slope of the log τ_w versus log $a_T B_{[\bar{M}_w]} \dot{\gamma}_w$ relationship is 1.0 in the shear stress region of 0 to 9.65×10^5 dynes/cm² (the lower Newtonian region), and the melt viscosity is therefore independent of shear rate in this region. The linear fit of the data in this region is given by the following equation:

$$\tau_w = C_1 (a_T B_{[\bar{M}_w]} \dot{\gamma}_w)^{D_1} \quad (3)$$

where $C_1 = \text{constant} = 0.0011$; $D_1 = \text{constant} = 1.0$ (Newtonian region); $a_T = \text{temperature shift factor, dimensionless, given by}$

$$a_T = F [\exp (E_a/RT)]; \ln a_T = -11.9755 + \frac{6802.1}{T} \quad (4)$$

$F = \text{constant}$; $\ln F = -11.9755$; $E_a = \text{activation energy of flow} = 13.5$ kcal/mole; $R = \text{gas constant} = 1.987$ cal/mole-°K; $B_{[\bar{M}_w]} = \text{molecular weight shift factor, dimensionless, given by}$

$$B_{[\bar{M}_w]} = G(\bar{M}_w)^J \quad (5)$$

$G = \text{constant} = 1.49 \times 10^{-15}$; $J = \text{constant} = 3.5$; $\bar{M}_w = \text{weight-average molecular weight}$; $\tau_w = \text{shear stress at wall, dynes/cm}^2$; and $\dot{\gamma}_w = \text{shear rate at wall (corrected), sec}^{-1}$.

Substituting and reducing yields

$$\eta_0 = \frac{\tau_w}{\dot{\gamma}_w} = 1.13 \times 10^{-13} \left[\left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right] (\bar{M}_w)^{3.5} \right] \quad (6)$$

where $\eta_0 = \text{zero shear viscosity, poises}$.

The following equation was used to relate $I.V.$ to \bar{M}_w ²⁰:

$$I.V. = 4.68 \times 10^{-4} (\bar{M}_w)^{0.68}. \quad (7)$$

Zero shear viscosity in terms of $I.V.$ is therefore

$$\eta_0 = \frac{\tau_w}{\dot{\gamma}_w} = 1.55428 \times 10^4 \left[\left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right] (I.V.)^{6.145} \right]. \quad (8)$$

Equations (6) and (8) are valid only for shear stresses $\leq 9.65 \times 10^5$ dynes/cm².

Intermediate Shear Stress Region ($9.65 \times 10^5 < \tau_w \leq 4.14 \times 10^6$ dynes/cm²). The flow behavior of PET melts above a shear stress of 9.65×10^5 dynes/cm² is pseudoplastic. The linear fit of the data in the shear stress range of 9.65×10^5 to 4.14×10^6 dynes/cm² (although the relationship is actually curved slightly) is given by the following equation:

$$\tau_w = C_2 (a_T B_{[\bar{M}_w]} \dot{\gamma}_w)^{D_2} \quad (9)$$

where $C_2 = \text{constant} = 0.01697$; $D_2 = \text{constant} = 0.707$; and $a_T, B_{[\bar{M}_w]}$, and $\dot{\gamma}_w$ are as defined previously. Substituting and reducing yield

$$\eta = 4.89132 \times 10^{-8} \left[\left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right] (\bar{M}_w)^{3.5} \right]^{0.707} (\dot{\gamma}_w)^{-0.293} \quad (10)$$

where $\eta = \text{melt viscosity, poises}$. In terms of $I.V.$ instead of molecular weight, eq. (10) becomes

$$\eta = 4.8569 \times 10^4 \left[\left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right]^{0.707} (I.V.)^{3.638} (\dot{\gamma}_w)^{-0.293} \right] \quad (11)$$

Equations (10) and (11) are valid only for the shear stress range $9.65 \times 10^6 < \tau_w \leq 4.14 \times 10^6 \text{ dynes/cm}^2$.

Melt Viscosity of PET

Graphic presentation of the melt viscosity of PET as a function of shear rate is made in Figures 1-3 for PET of 0.55, 0.60, and 0.65 $I.V.$, respectively. Similar graphs for PET of other $I.V.$ values can be constructed from data derived from eqs. (8) and (11). Isotherms are shown as solid lines, the dashed lines represent constant shear stress, and the dashed line with triangles (\blacktriangle) is the constant stress boundary for departure from Newtonian behavior (to be discussed in a paper to be published later). Note that as $I.V.$ increases, the region of Newtonian behavior narrows (departure from Newtonian behavior occurs at lower shear rates) and lengthens (the effect of

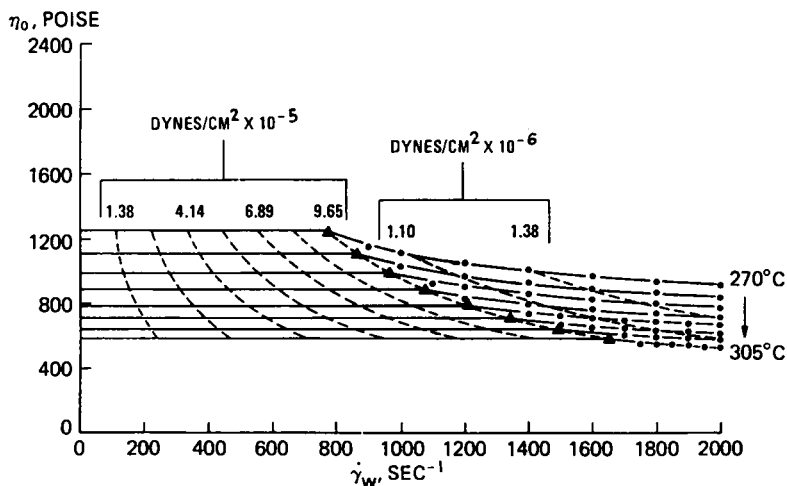


Fig. 1. Melt viscosity as a function of shear rate for poly(ethylene terephthalate) of 0.55 $I.V.$: (—●—) constant T ; (----) constant τ_w ; (—▲—▲—) departure from Newtonian behavior.

temperature on viscosity increases). A three-dimensional graph of melt viscosity–shear rate– $I.V.$ could be constructed and certainly can be visualized; Figures 1–3 are three planes of constant $I.V.$ in such a three-dimensional construction.

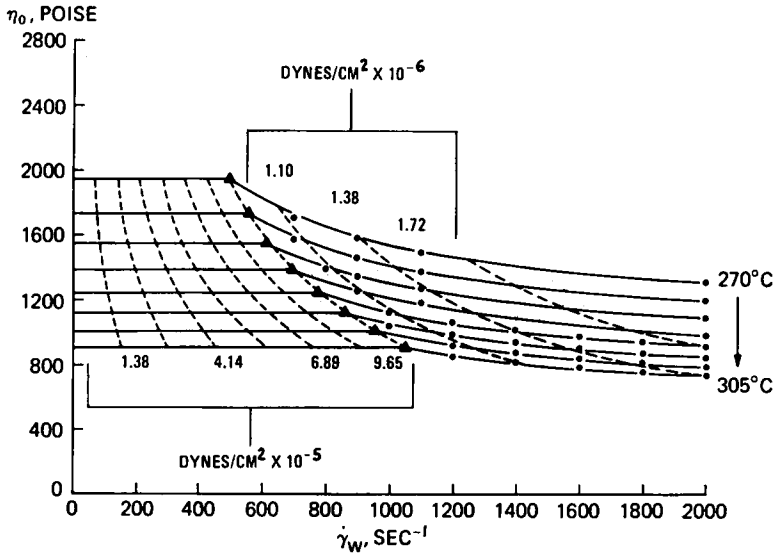


Fig. 2. Melt viscosity as a function of shear rate for poly(ethylene terephthalate) of 0.60 $I.V.$: (—●—) constant T ; (----) constant τ_w ; (—▲—▲—) departure from Newtonian behavior.

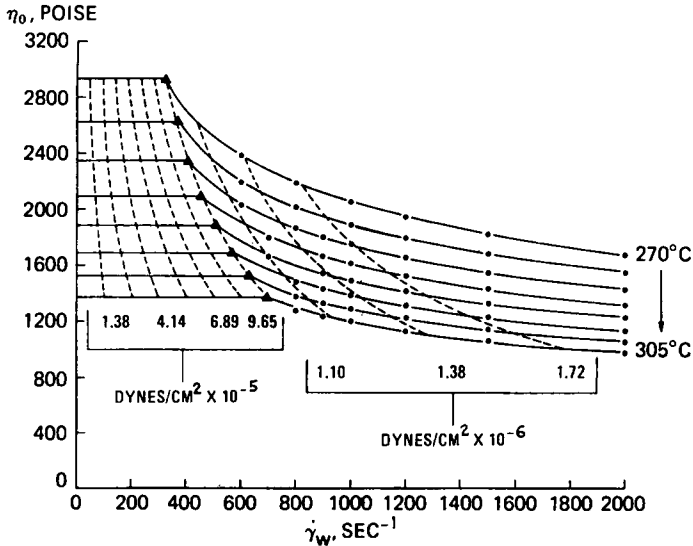


Fig. 3. Melt viscosity as a function of shear rate for poly(ethylene terephthalate) of 0.65 $I.V.$: (—●—) constant T ; (----) constant τ_w ; (—▲—▲—) departure from Newtonian behavior.

Effect of Temperature Changes on Melt Viscosity

The effect of a unit temperature change on the Newtonian melt viscosity of molten PET is given by the first derivative with respect to temperature of eq. (8):

$$\frac{d\eta_0}{dT} = -1.05724 \times 10^8 (I.V.)^{5.145} \left[\exp \left(-11.9755 + \frac{6801.1}{T} \right) \right] \left(\frac{1}{T^2} \right). \quad (12)$$

The rate of change of viscosity with temperature ($d\eta_0/dT$) increases with increasing $I.V.$ for a given temperature and decreases with increasing temperature for a given $I.V.$ The percentage change in melt viscosity for a change in temperature is independent of $I.V.$ level but decreases slightly with increasing temperature.

Effect of $I.V.$ Changes on Melt Viscosity

The first derivative of eq. (8) with respect to $I.V.$ yields the effect of a unit $I.V.$ change on the Newtonian melt viscosity of PET:

$$\frac{d\eta_0}{d(I.V.)} = 7.99677 \times 10^4 (I.V.)^{4.145} \left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right]. \quad (13)$$

The rate of change of viscosity with $I.V.$ [$d\eta_0/d(I.V.)$] increases with increasing $I.V.$ for a given temperature and decreases with increasing temperature for a given $I.V.$ The percentage change in melt viscosity for a change in $I.V.$ is independent of temperature but increases considerably with decreasing $I.V.$ For PET of 0.60 $I.V.$, a 0.0025 change in $I.V.$ accounts for about the same change in melt viscosity as a 1°C change in temperature.

Comparisons With Previously Reported Data

Other investigators have reported melt viscosity data for PET.⁷⁻¹⁰ Comparisons of results of this investigation with results of each of the other investigations were made and are included in Table I. The results of this investigation agree reasonably well with the earlier data of Martin and Kibler,⁹ Schulken,¹⁰ and Manaresi et al.⁷ Data of Petukhov⁸ show considerable deviation from those of this investigation, especially at low temperatures and high molecular weights. He used a falling-ball viscometer (a poor choice for melts) which should perform poorly at low temperatures and high molecular weights. In fact, he reported that he could not measure the melt viscosity of 0.74 $I.V.$ polymer.

Sufficient agreement exists between data of several other investigators^{7,9,10} (taken over a wide range of experimental conditions when all are considered collectively) and the comprehensive data of this paper to solidify confidence in the results reported here. Complete description of the steady-state flow behavior of molten PET (over a wide range of $I.V.$, temperature, and shear rate) has been achieved.

TABLE I
Comparison of Results of This Investigation on PET Melt Viscosity With Those of Previous Investigations

Reference Source	Author	Inherent Viscosity	T, °C	η_0 , Poise		Difference, %
				Other Investigation	This Investigation ^a	
7	Manaresi et al.	0.36	280	126	113	+11.5
		0.41		251	222	+13.1
		0.56		1073	1087	- 1.3
		0.63		2092	2020	+ 3.6
		0.79		6930	6470	+ 7.1
8	Petukhov	0.54	270	850	1166	-27.1
		0.58		2800	1579	+77.3
		0.59		3400	1818	+87.0
		0.66	4300	3059	+40.6	
		0.74	Did not flow	5933	-	
		0.54	280	500	930	-46.2
		0.58		1200	1260	- 4.8
		0.59		2150	1450	+48.3
		0.66	3100	2440	+27.0	
		0.74	Did not flow	4730	-	
		0.54	290	420	747	-43.8
		0.58		950	1012	- 6.1
		0.59		1200	1165	+ 3.0
		0.66	2000	1960	+ 2.0	
		0.74	Did not flow	3800	-	
9	Martin and Kibler	0.60	278	1800	1626	+10.7
		0.70		3700	3587	+ 3.2
		0.80		7000	7135	- 1.9
10	Schulken	0.30	260	77	70	+10.6
		0.29		37	37	0.0
		0.42		118	248	-52.4

^a Values calculated from eq. (8) derived from the experimental data of this investigation.

CONCLUSIONS

The complete steady-state flow properties of molten PET for shear stress $\leq 4.14 \times 10^6$ dynes/cm² were defined. This work now makes possible the direct calculation of the melt viscosity of PET for shear stresses $\leq 4.14 \times 10^6$ dynes/cm².

The temperature shift factor a_T , and thereby the activation energy of viscous flow E_a , were shown to be independent of molecular weight for PET within experimental error. The molecular weight shift factor $B_{[M\dot{\omega}]}$ was shown to be independent of temperature within experimental error.

The rate of change of viscosity with temperature, $d\eta_0/dT$, increases with increasing $I.V.$ for a given temperature and decreases with increasing temperature for a given $I.V.$ The percentage change in melt viscosity for a

change in temperature is independent of $I.V.$ level but decreases slightly with increasing temperature.

The rate of change of viscosity with $I.V.$, $d\eta_0/d(I.V.)$, increases with increasing $I.V.$ for a given temperature and decreases with increasing temperature for a given $I.V.$ The percentage change in melt viscosity for a change in $I.V.$ is independent of temperature but increases considerably with decreasing $I.V.$ For polymer of 0.60 $I.V.$, a 0.0025 change in $I.V.$ accounts for about the same change in melt viscosity as a 1°C change in temperature.

The comprehensive results of this paper agree reasonably well with the data obtained in scattered regions of interest by several other authors.

References

1. D. R. Gregory and M. T. Watson, *J. Polym. Sci. C*, **30**, 399 (1970).
2. R. A. Mendelson, *Trans. Soc. Rheol.*, **9**, (1), 53 (1965).
3. R. A. Mendelson, *SPE Trans.*, **5**, 34 (1965).
4. R. A. Mendelson, *Polym. Letters*, **5**, 295 (1967).
5. F. Bueche and S. W. Harding, *J. Polym. Sci.*, **32**, 177 (1958).
6. T. G. Fox and P. J. Flory, *J. Polym. Sci.*, **14**, 315 (1954).
7. P. Manaresi, E. Giachetti, and E. De Fornasari, *J. Polym. Sci. C*, **16**, 3133 (1968).
8. B. V. Petukhov, *The Technology of Polyester Fibres*, MacMillan, New York, 1963, p. 34.
9. E. V. Martin and C. J. Kibler, in *Man-Made Fibers*, Vol. 3, H. F. Mark, S. M. Atlas, and E. Cernia, Eds., Interscience, New York, 1968.
10. R. M. Schulken, unpublished information.
11. E. H. Merz and R. E. Colwell, *ASTM Bull.*, **32**, 117 (1958).
12. J. S. Perlowski, R. D. Coffee, and R. B. Edwards, U.S. Pat. 3,330,809 (1967).
13. C. J. Kibler, A. Bell, and J. G. Smith, *J. Polym. Sci. A*, **2**, 2115 (1964).
14. J. Ferguson, B. Wright, and R. N. Haward, *J. Appl. Chem.*, **14**, 53 (1964).
15. A. K. Van der Vegt, *J. Trans. Plast. Inst.* (London), **33**, 265 (1964).
16. W. J. Bontinck, *Ind. Plast. Mod. Elastomere*, **18**(10), 121 (1966).
17. E. M. Aizenshtein and B. V. Petukhov, *Khim. Volokna*, **4**, 20 (1964).
18. I. Marshall and A. Todd, *Trans. Faraday Soc.*, **49**, 67 (1953).
19. G. V. Vinogradov and N. V. Prozorovskaya, *Sov. Plast.*, 4144 (1967).
20. L. D. Moore, Jr., private communication.

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