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A STUDY OF THE VISCOSITY OF THORIA SOLS

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ABSTRACT

In a preliminary investigation, effects of aging, shear rate, thoria concentration, and nitrate concentration on the viscosity of carefully prepared sols of oxalate ThO_2 dispersed in dilute HNO_3 solutions by the sol-gel process were studied. The ThO_2 sols were non-Newtonian, thixotropic, and rheopectic. The viscosity increased with relative age at low, constant rates of shear; the effect decreased as rates of shear increased and reversed at high shear rate. Equilibrium viscosities were approached with aging for each shear rate whether rates of shear were increased stepwise or decreased. Viscosities increased sharply with increasing NO_3^-/ThO_2 mole ratios at all rates of shear.

INTRODUCTION

The purpose of this exploratory study was to determine, for nitrate-stabilized suspensions of oxalate-precipitated thoria in water the effects of thoria concentration, nitrate concentration, and time on their viscosity.

In the development of the sol-gel process for preparation of high-density thoria and uranium thorium oxide fuel particles (1,2), widely varying rheological behavior, Newtonian and non-Newtonian, was qualitatively observed for colloidal suspensions of thoria in water containing nitrate ions. The causes for variation appeared to be the source of thoria, thoria concentration, nitrate concentration, temperature and age of suspension. Since successful applications of the sol-gel process depend on accurate prediction and the control of flow of sols and setting of gels, information is needed on how the above variables affect the apparent viscosity of thoria-water-nitrate suspensions.

The viscometry of thoria suspensions by other investigators (3-7) was carried out with alkali-precipitated hydrous oxides, and with the exception of Dhar and Mittra (5), with very dilute thoria suspensions. Dobry (7) dialyzed precipitated thoria sols to explore electroviscous effects at concentrations up to 2 wt % ThO_2, and encountered complex behavior believed to be due to the unwinding of linear polymer species.

In the present study the thoria source was limited to oxalic acid-precipitated from 30°C thorium nitrate solution, thoroughly digested at 85°C, 48 hr, and washed and calcined at 800°C, 4 hr. The reason for selection of a well crystallized species was to eliminate variables other than those to be studied which might affect viscosity, i.e., wide crystallite size distribution and chemical impurities. The range of ThO_2 concentrations studied was 2-3 molar, since this is the range of interest in the sol-gel process. The effect of NO_3^-/ThO_2 mole ratio was studied over the range of 0.042 to 0.048. Aging effects over a 100-hr range were studied for four different rates of shear.

Apparatus, Materials, and Methods. A Brookfield Multi-speed Model LVT Viscometer, Serial No. 6956, was used for all viscosity measurements in this study. This is a Couette-type with stationary outer cylinder and rotating inner cylinder or spindle. The viscometer is equipped with four spindles identified as No. 1, 2, 3, and 4. Spindle No. 1 was used in all measurements except those on sols ES3EVA and ES3EVB. The spindle could be rotated at four different speeds—6, 12, 30, and 60 revolutions per minute. This afforded a means of studying the viscosity with rate of shear and is therefore a means of classifying the sol as to type of behavior.

All measurements were made in a constant temperature bath of mineral oil regulated to $25.0 \pm 0.1^{\circ}$. The sol was placed in a 250 ml tall form beaker and then in the bath for at least an hour before each measurement. To minimize evaporation an aluminum cover was placed over the beaker on all sols except ES1A.

The viscometer was checked for accuracy using glycerol-water solutions. The densities of the solutions were measured using a chain-o-matic density balance. The percentage composition was then obtained from tables of density vs percentage composition. The results are listed below (all measurements at 25°C): From this it is seen that the viscometer is reliable at viscosities above 20 centipoises and will give acceptable values at lower viscosities. This standardization was made on the No. 1 spindle.

Table 1. Calibration of Viscometer

Fluids, Glycerol-Water Solutions of Varying Composition

Solution	Density	Composition, wt % glycerine	Viscosity, centiposies	
			Calculated	Measured Mean
1	1.2473	95.8	420	423
2	1.1660	65.9	13.1	13.9
3	1.1651	65.1	12.5	13.2
4	1.1194	48.4	4.7	6.8

Materials: Sol Preparation. All sols were prepared from oxalate oxide-DT 31 by adding HNO_3 followed by a double evaporation at 135° and then suspending in a desired amount of water. The following table describes the sols used in this study:

Table 2. Properties of Thoria Sols

Sol	Approx. Molarity	Density	NO_3/ThO_2, Mole Ratio	pH
ES1A	3	1.643[a]	0.0421	2.22[a]
ES3EV	2	1.482	0.0420	2.40
ES3EVA[b]	2	-	0.0424	2.28
ES3EVB[c]	2	-	0.0428	2.12
ES9	2	1.421	0.0480	2.38

[a] Average value-increased during measurements.
[b] Prepared from 205 ml of ES3EV by adding o.1 ml of 15.8 M HNO_3.
[c] Prepared from 194 ml of ES3EVA by adding 0.1 ml of 15.8 M HNO_3.

Methods of Measurement of Apparent Viscosities. The apparent viscosity of all of the sols studied varied with time for and constant rate of shear at constant time. Although viscosities never became truly constant for any rate of shear, it was possible to establish essentially equilibrium values within a reasonable time (Figs. 1 and 2). Switches from one viscometer rate to another gave the same equilibrium value at the same shear rate for the same sol whether rates were varied in ascending or descending order (Fig 3).

Experimental Results. The most complete work was done on sols ES1A, ES3EV, and ES9. A summary of the data from these sols is given in Table 3. The viscosities listed are the equilibrium values determined as previously described. The densities were measured with a chain-o-matic density balance and the pH with a Beckman (6) pH meter. The age of the sol is determined relative to the time of the first viscosity measurement.

Rheological Classification of ThO_2 Sols. Previous work on ThO_2 sols (1,2) indicate that they are pseudoplastic in their behavior. Plots of the viscosity vs rates of shear given in Figs. 4, 5, and 6 indicate non-Newtonian thixotropic behavior with an extreme, perhaps even asymptotic, rate of

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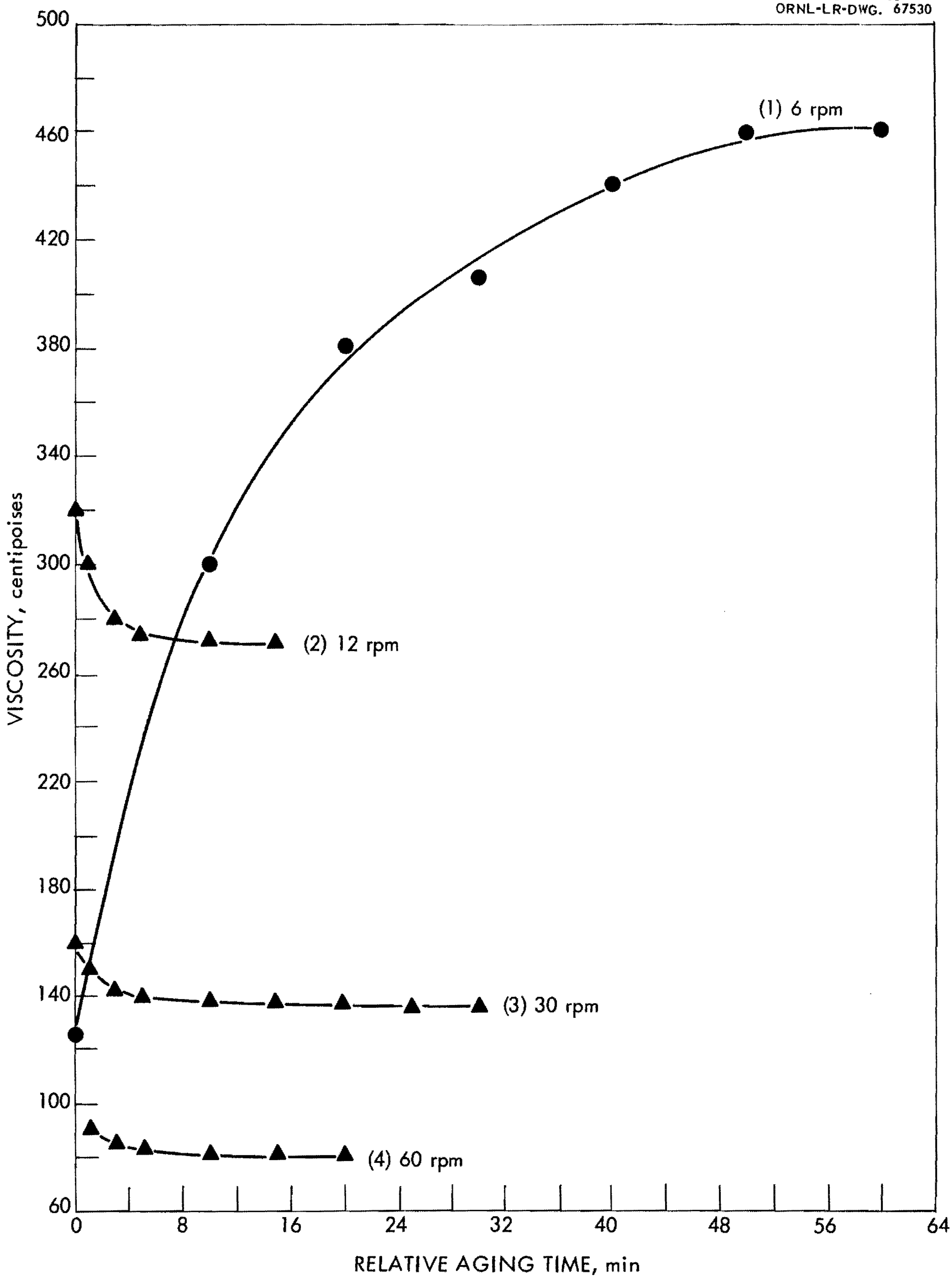

Fig. 1. Variation of viscosity of ThO_2 sol with time at four different shear rates. Shear rates changed in ascending order. Numbers in parentheses indicate order of measurement.

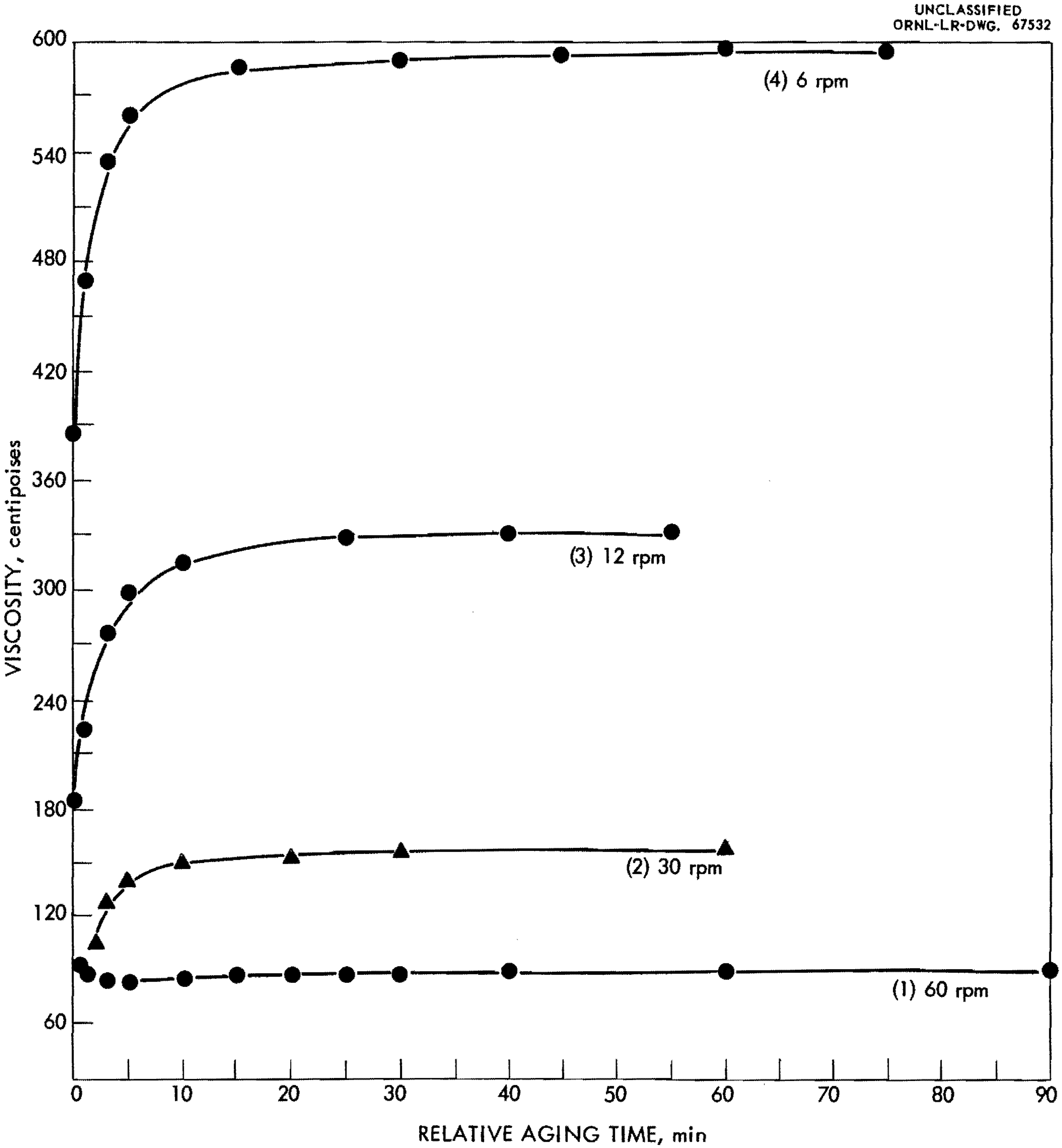

Fig. 2. Variation of viscosity with time at four different shear rates. Shear rates changed in descending order. Sol ES1A (Run 4) - 7-20-61. Density = 1.65, pH = 2.32. Numbers in parentheses indicate order of measurement.

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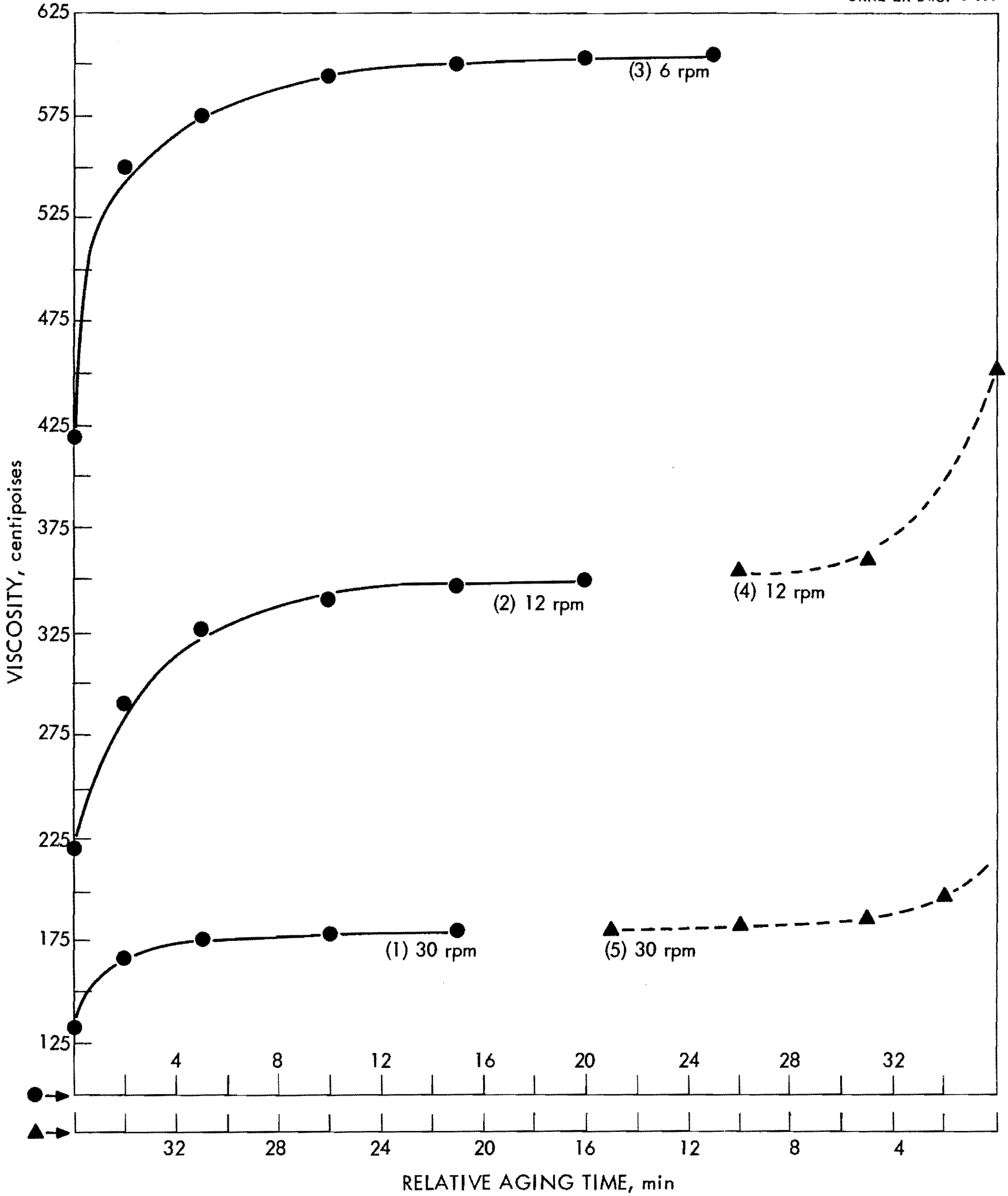

Fig. 3. Effect of time on viscosity at constant shear rate. ES3EV (Run 3). Numbers in parentheses indicate order of measurement.

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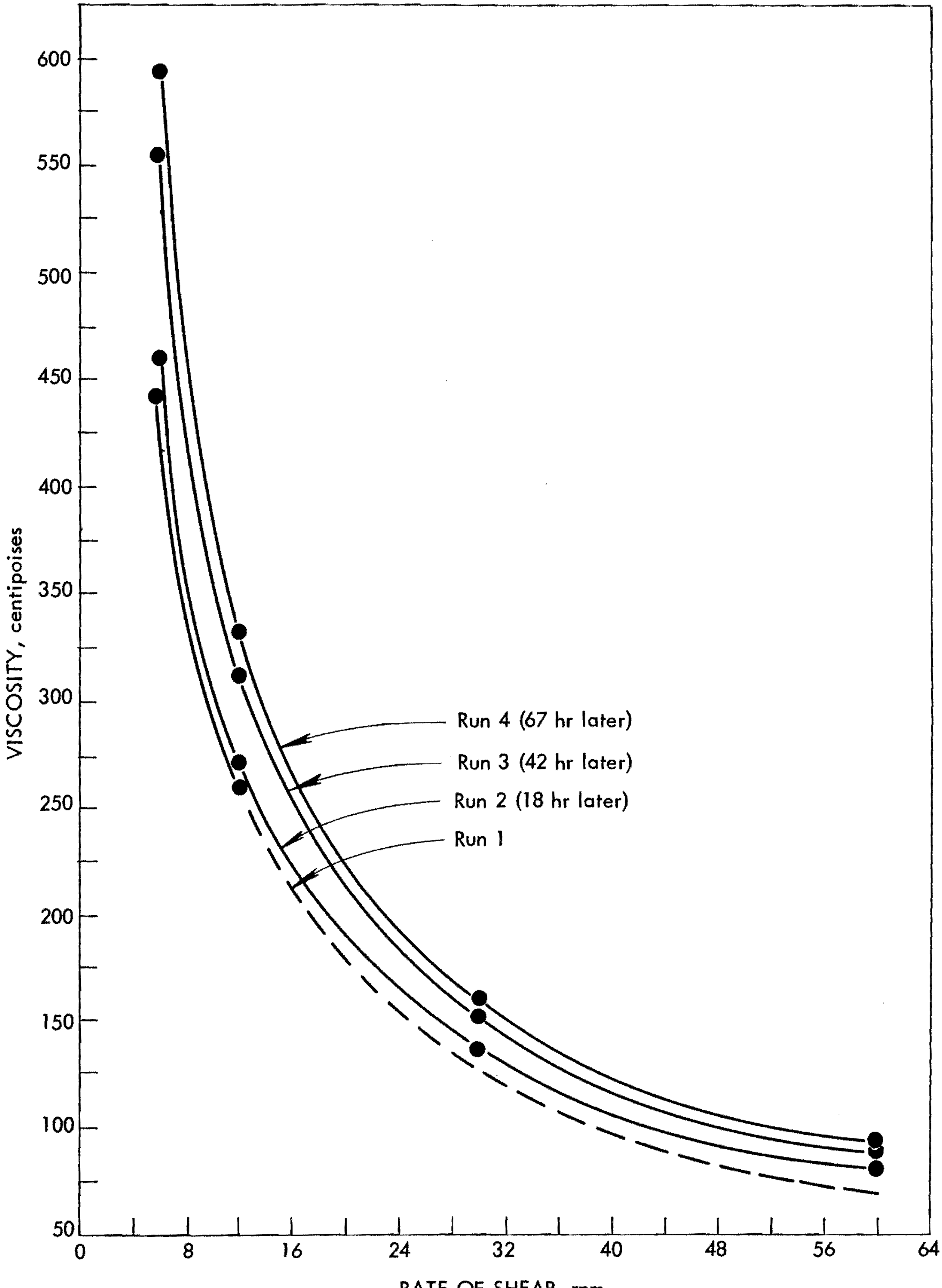

Fig. 4. Viscosity vs rate of shear at four relative ages for sol ES1A.

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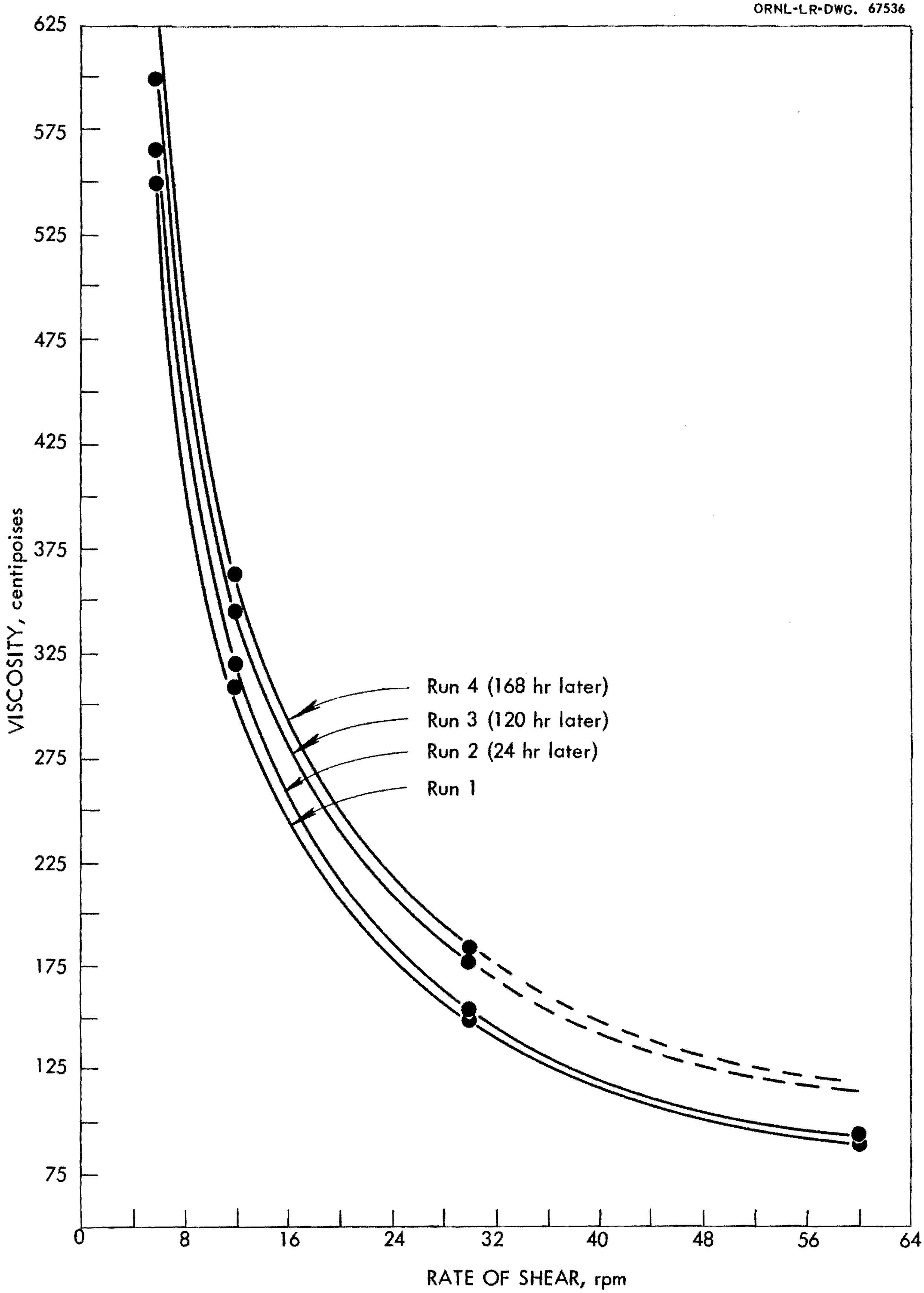

Fig. 5. Viscosity vs rate of shear at four relative ages for sol ES3EV.
Density = 1.482, pH = 2.40 for all runs.

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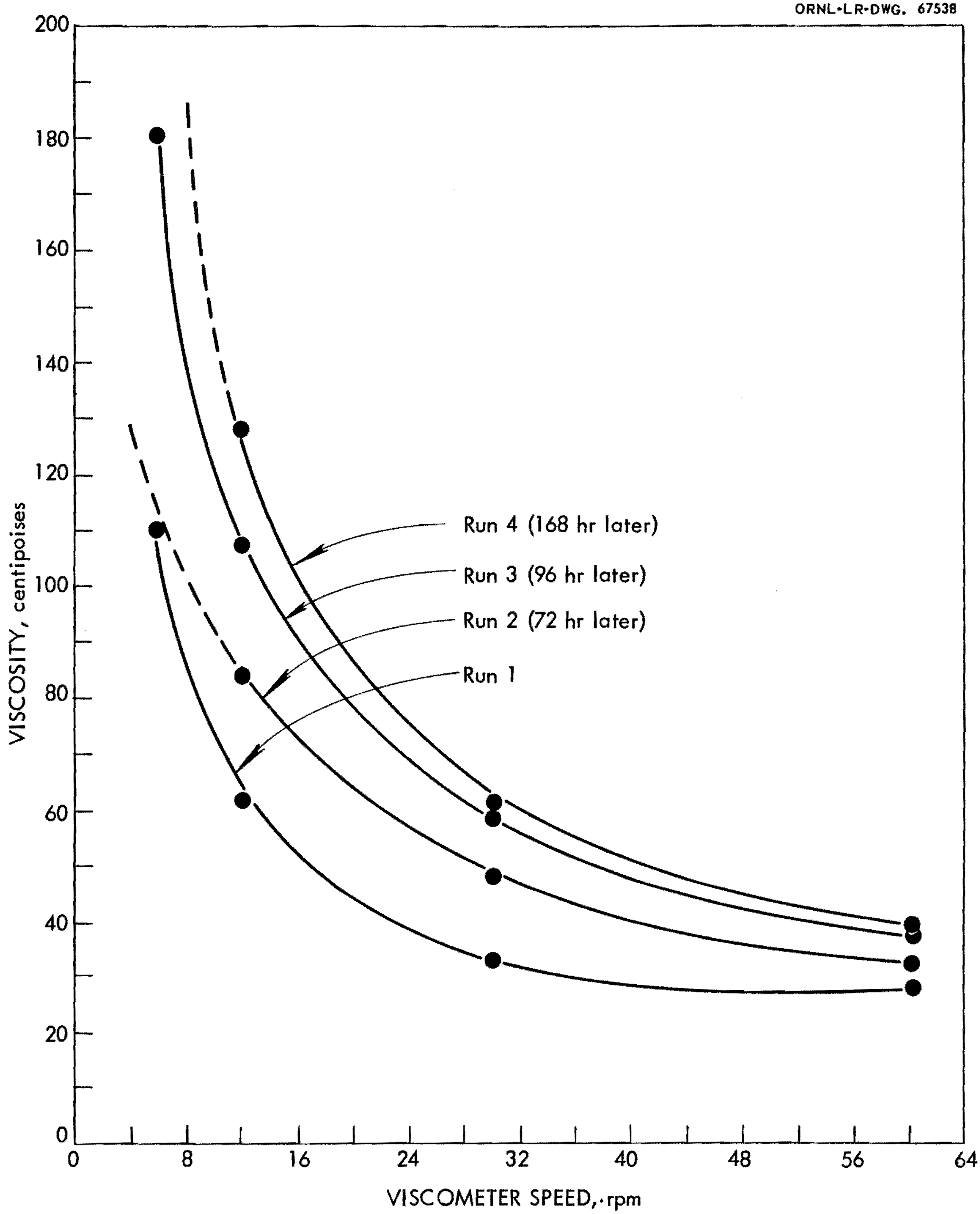

Fig. 6. Viscosity vs rate of shear at four relative ages for sol ES9.

increase of viscosity at low rates of shear. This behavior was shown to be very reproducible for different sols and for varying ages of the same sol. The effect of changing rate of shear on apparent viscosity is similar for the range of densities, pH and age of sol used in this study.

Table 3. Densities, pH, and Variation of Viscosity with Rates of Shear and Sol Age for Three Thoria Sols

Run No.	Apparent Viscosity, centipoises 6 rpm	12 rpm	30 rpm	60 rpm	Density, g/cc	pH	Relative Age, hr
			Sol Preparation ES1A				
1	442	260	-	-	1.639	2.12	0
2	460	271	135	80	1.639	2.19	18
3	555	314	150	88	1.643	2.26	42
4	594	331	158	90	1.647	2.32	67
			Sol Preparation ES3EV				
1	550	310	148	88	1.482	2.40	0
2	567	318	151	90	1.481	2.40	24
3(a)	605	349	178	>100	1.482	2.40	120
(b)	596	342	176	>100	-	-	124
4	632	362	180	>100	1.482	2.40	168
			Sol Preparation ES9				
1	110	62	33	28	1.411	2.42	0
2	-	84	48	32	1.421	2.36	72
3	180	107	58	37	1.425	2.38	96
4	-	128	61	39	-	-	168

Aging Effects. Viscosity increases with the age of the sol (Table 3, Figs. 7, 8, 9). This effect has been observed before (5). The rate of this increase with age is more pronounced at lower rates of shear. This is indicated by the increasing slopes of the plots from 60 down to 6 rpm.

Other aging effects are apparent from Table 3. In sol ES1A and ES9 the densities increased with time and in ES1A, the pH decreased. The pH change in ES9 is inconclusive. ES3EV showed no change in density over a period of 7 days while the viscosity was increasing steadily. It is significant that the "pH" of this sol also remained unchanged during

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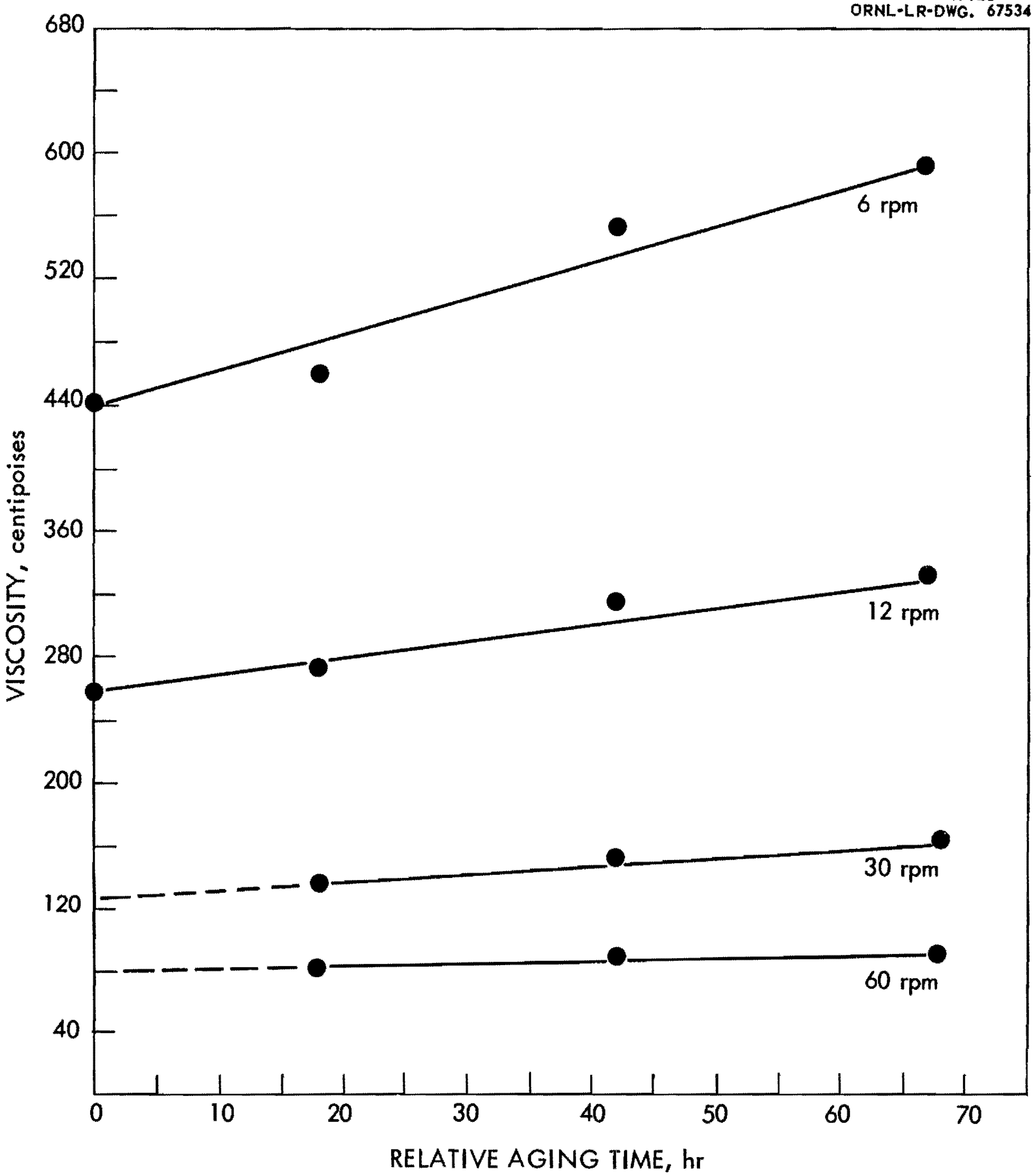

Fig. 7. Effect of time on viscosity of ThO_2 sols at four rates of shear. ES1A.

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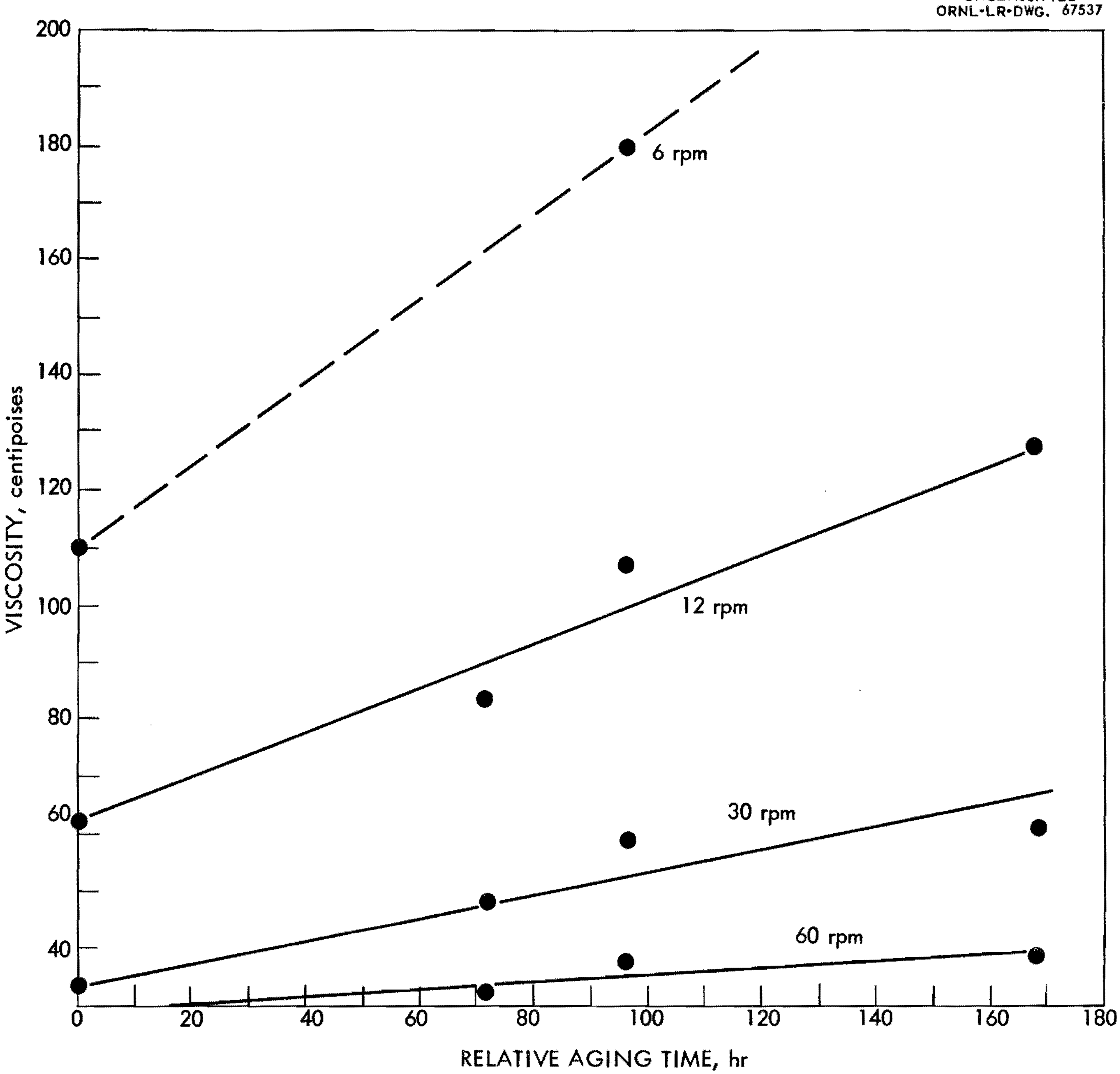

Fig. 8. Effect of time on viscosity of ThO_2 sols at four rates of shear for sol ES9.

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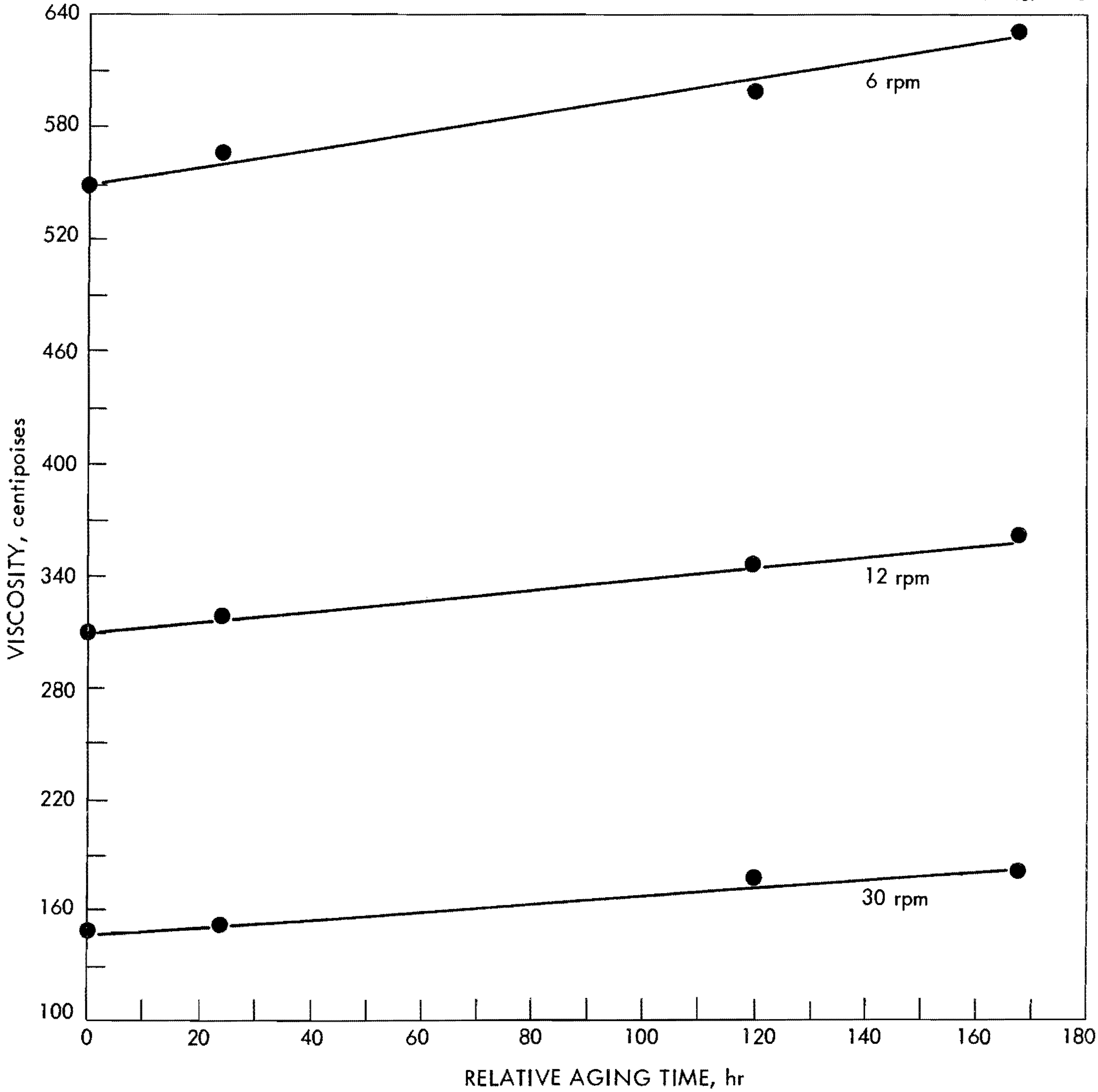

Fig. 9. Effect of time on viscosity of ThO_2 sols at three rates of shear. ES3EV.

this 7 day period. The only significant difference in preparative procedure for ES3EV and the other two sols was that it was prepared by evaporating a less concentrated sol to about one-half volume.

Table 4 summarizes and compares viscosities of sols ES1A, ES3EV, and ES9 at approximately equal times from date of preparation. Since ES3EVA and ES3EVB were prepared from ES3EV their ages are greater than those of the other three. However, for the purposes of comparison the effect of aging can be estimated from Table 6, which is calculated from the data in Table 3.

Electroviscous Effect. Additional work was done on sol ES3EV in an attempt to determine, quantitatively, the effect of nitrate. Sol ES3EVA and ES3EVB were prepared from ES3EV by successive additions of 0.1 ml of 15.8 M HNO_3. Although data was limited (Table 6) it was observed for the three sols of series ES3EV that there was a definite increase in viscosity with added nitrate, even when calculated aging effects (Table 5) were subtracted out.

Table 4. Aging Effects: Apparent Viscosity of Various Sols at Comparable Times from Preparation[a]

Sol	Time from Prep'n.	NO_3/ThO_2, mole ratio	Density, g/cc	pH	Viscosity, cp, at various rates of shear, rpm: 6	12	30	60
ES1A (Run 3)	9 days	0.0421	1.643	2.26	555	314	150	88
ES3EV (Run 3)	10 days	0.0420	1.482	2.40	600	345	177	>100
ES3EVA	17 days	0.0424	-	2.28	965	530	265	160
ES3EVB	19 days	0.0428	-	2.12	1420	820	380	220
ES9 (Run 3)	8 days	0.0480	1.425	2.38	180	107	58	37

[a]Compare ES1A, ES3EV, and ES9 and ES3EVA with ES3EVB.

Table 5. Effect of Aging on the Apparent Viscosity of Sols

Sol	Aging Factors, centipoises/day			
	6	12	30	60
ES1A	51	24	12	5
ES3EV	10	6	4	2
ES9	17	9	4	2

Table 6. Effects of Increasing NO_3/ThO_2 Ratio on Apparent Viscosity of ThO_2 Sols

Sol	Viscosity, centipoises				pH	NO_3/ThO_2	Relative Age, hr
	6	12	30	60			
ES3EV	632	362	180	>100	2.40	0.0420	0
ES3EVA	965	530	265	160	2.28	0.0424	96
ES3EVB	1420	820	380	220	2.12	0.0428	144

Dhar and Mittra (5) reported that the relative viscosity of ThO_2 sols peptized with $Th(NO_3)_4$ varied with the molar ratio of nitrate to thorium. In a plot of increasing M_{NO_3}/M_{Th} vs viscosity, the viscosity decreased to a minimum at approximately 0.3 M_{NO_3}/M_{Th}, then increased. The reason for the apparent contradiction is not known, except that the thoria sources and peptizing agents were very different. In this study also it appeared that apparent viscosity increased with decreasing pH. It is not known, however, if variation in pH is merely a response to added nitrate or if it is a cause for variation of the viscosity.

Effects of ThO_2 Concentration. Dhar and Mittra (5) concluded that relative viscosity of thoria sols increased linearly with ThO_2 concentration. In this study an attempt was made to measure ThO_2 concentration by sol density. Measurements on ES1A and ES9 sols (Table 3) showed that density increased with aging, while the gross concentration of ThO_2 in the system remained constant. This fact makes density an unreliable measure of concentration, and hence no statement based on data in this study would be meaningful.

CONCLUSIONS AND DISCUSSION

The behavior of the ThO_2 sols, studied in this system, is definitely non-Newtonian and thixotropic.

There is a definite electroviscous effect of increasing viscosity with small amounts of added nitrate.

There is no simple correlation between density of a sol and its ThO_2 concentration; the density is apparently a function of ThO_2 concentration, nitrate content, and age.

A study of Fig. 3 indicates a structure formation in ThO_2 sols under shear. The viscosity increases to an equilibrium value at each rate of shear as the speeds are decreased stepwise from 30 to 6 rpm. Reversal of this process, increasing speeds from 6 to 30, gives the same equilibrium value. This could be interpreted (8,9) as being due to structure formation (rheopexy), the amount varying inversely with the rate of shear. As the speeds are decreased, the structure becomes more definite. Upon increasing speeds, the structure is partly destroyed resulting in a decrease in viscosity. On standing for a few minutes the viscosity will once again start at a low value and increase with time for a given rate of shear, indicating that the structure formed by shearing is weak enough to be disrupted by ordinary thermal forces at 25°C.

The aging process can be ascribed to a combination of effects. First the discussion above indicated that the sol structure is perhaps polymeric, the chains being aligned by shear and recoiling when the shear is removed. The aging process therefore could be partly due to growth of the chains causing the structure to become more rigid with time.

Another aging effect may be due to the adsorption of CO_2 from the air since ThO_2 is known to adsorb CO_2 strongly.

Both of these processes should result in release of nitrate to the liquid surrounding the sol and therefore a corresponding increase in conductivity of the sol. This increase in conductivity with age has been observed by Dhar and Mittra (5).

RECOMMENDATIONS FOR EXTENDED STUDIES

It is believed that an extensive study of the rheological behavior of ThO_2 sols combined with experiments on light scattering would provide a means of proposing a structure for the sol and the mechanisms of its stabilization. Studies which would be of value are:

(1) Study of the aging process by controlled environment with measurements of viscosity and conductivity over an extended period.

(2) Detailed study of quantitative dependence of viscosity upon nitrate content and ThO_2 concentrations.

(3) Experiments designed to study the adsorption mechanism on ThO_2.

(4) Light scattering experiments designed to measure (or calculate) sol particle size.

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