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Use of the Hysteresis Loop Method to Study Thixotropic Suspensions

Part 2 - Acetylene Black in Hydrazine and Pyrogenic Silica in Liquids of Varying Polarity

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ABSTRACT

The hysteresis loop method was used to study the flow properties of suspensions of acetylene black in hydrazine and of pyrogenic silica in n-decane, hydrazine, unsymmetrical dimethylhydrazine, n-propyl and isopropyl alcohols, and water. It was found that the acetylene black/hydrazine system behaved ideally, in that the plastic viscosity and yield stress values of these suspensions followed Arrhenius' law at low concentrations and Weltman and Green's equation at higher concentrations.

Of the silica suspensions tested, only the pyrogenic silica/n-decane system exhibited the same exponential dependence of plastic viscosity and yield stress on concentration as was found for the ideal thixotropic suspensions. The remaining silica suspensions either broke down irreversibly under high shear conditions or were otherwise unsuitable for study by the hysteresis loop method.

PROBLEM STATUS

This is a final report on one phase of the problem; work on other phases is continuing.

AUTHORIZATION

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USE OF THE HYSTERESIS LOOP METHOD TO STUDY THIXOTROPIC SUSPENSIONS

PART 2 -- ACETYLENE BLACK IN HYDRAZINE AND PYROGENIC SILICA IN LIQUIDS OF VARYING POLARITY

INTRODUCTION

It has been suggested that the hazards involved in storage and handling of liquid propellants aboard ship could be substantially reduced by converting the liquids to thixotropic gels. In addition, such gels would provide a means of suspending high-energy metals and solids in the fuel to bring about an overall increase in the specific impulse of the system (1).

Previous work at NRL has shown that the hysteresis loop method is an effective means of studying an ideal thixotropic gel system (2). Briefly, this method depends on the fact that when a thixotropic gel is placed in a cup and bob type viscometer, and the shear rate increased rapidly to a preselected maximum and then decreased to zero, a plot of the shear stresses encountered along the way forms a hysteresis loop. From this loop, the following data points are obtained:

τ_0, experimental yield stress, a measure of the minimum yield stress that must be overcome before flow will commence

τ_B, Bingham yield value, obtained by extrapolating the straight-line portion of the upcurve

$\tau_{D_{max}}$, shear stress at maximum shear rate

τ_{ext}, extrapolated yield stress, obtained by extrapolating the straight-line portion of the downcurve

τ_N, residual gel strength, a measure of the amount of structure remaining in the gel after it has undergone the shear history as given by the upcurve and downcurve.

In describing the flow properties of gels, the term plastic viscosity is frequently used, since Newtonian or apparent viscosities, which are merely the ratio of shear stress to shear rate, are meaningless when applied to gels.

The plastic viscosity, η_{pl}, at the maximum shear rate, D_{max}, may be calculated from the formula:

$$\eta_{pl} = \frac{\tau_{D_{max}} - \tau_{ext}}{D_{max}} \tag{1}$$

where

η_{pl} = plastic viscosity, poise

D_{max} = maximum shear rate, sec^{-1}.

In the previous study (2), it was found that for an ideal thixotropic gel, namely, Ben-a-gel in water, the plastic viscosity could be related to concentration by either of two exponential laws. At low concentrations, in the so-called pregelation region, the suspensions followed Arrhenius' law, i.e.,

$$\eta_{pl} = \eta_0 e^{kC} \tag{2}$$

where

η_0 = viscosity of suspending liquid, poise

k = constant

C = concentration, vol-%.*

At higher concentrations, in the postgelation region, Weltmann and Green's equation was found to apply, i.e.,

$$\eta_{pl} = (\eta_0 + A) e^{BC} \tag{3}$$

where

A and B = constants

C = concentration, vol-%.

Also, it was found that the yield points, τ_B, τ_{ext}, and τ_N, could be related to concentration by using the equation:

$$\tau = M e^{NC} \tag{4}$$

where

τ = yield stress, dynes/cm^2

M = yield stress intercept

N = the slope

C = concentration, vol-%.

When the yield-stress data for the Ben-a-gel/water system were plotted according to Eq. (4), a break in the curve was also found at the point marking the transition from thixotropic liquid to gel.

In the present study, an attempt was made to determine if the preceding equations could be applied to gelled propellant systems. The liquid propellants used in this study were hydrazine and unsymmetrical dimethylhydrazine (UDMH). A variety of organic and inorganic gelling agents were screened, but only two were selected for rheological studies with hydrazine and UDMH: acetylene black and pyrogenic silica. Suspensions of these gelling agents were examined by the hysteresis loop method using both a low shear and a high shear cup and bob combination. Sample concentrations covered the range from thixotropic liquid to gel.

*In a true Arrhenius plot, concentration is expressed as grams of solid per cc of suspending liquid. For uniformity, vol-% was used in this study.

In addition, studies were made of the gelling ability of pyrogenic silica as a function of particle size in liquids of varying polarity, with the purpose of determining optimum conditions for gelation with this agent.

EXPERIMENTAL DETAILS

Screening of Gelling Agents

In most cases, the candidate gelling agent was added gradually to 100 ml of the liquid propellant while stirring with an ordinary, propeller-type, lab stirrer at approximately 1200 rpm. However, certain gelling agents, e.g., the bentones and hydrogenated castor oil, were known to require high shear mixing to develop maximum properties. Suspensions of these gelling agents were prepared by stirring in a Waring Blendor for two minutes.

Preparation of Samples for Rheological Studies

A Premier Dispersator, Type SSD, with duplex head, was used to make the acetylene-black dispersions. It was found that this unit produced stronger gels with acetylene black and hydrazine than the Waring Blendor. The samples were stirred for five minutes at a Variac setting of 30 v for the less concentrated suspensions (2.62 vol-% or less) and at 40 v for the more concentrated samples.

Suspensions of pyrogenic silica in n-decane, n-propyl, and isopropyl alcohols and in UDMH were prepared in a two-speed Waring Blendor. The suspension was sheared for two minutes at low speed, or until the material gelled. If a sample gelled, it was shaken down into the path of the blades and sheared again until it set up. The shaking down and shearing procedure was continued for ten cycles, after which the gel set up so rapidly that further shearing was unnecessary.

Since suspensions of pyrogenic silica in hydrazine and in water tended to be completely broken down with high shear mixing, an ordinary, propeller-type, lab stirrer was used for these samples.

Rheological Studies

The hysteresis loop method was used for studying the rheological behavior of the suspensions. Details on this procedure and of the apparatus are given in the previous report (2).

SCREENING STUDIES

The criterion of an acceptable gelling agent used in this study was that the agent must form a stable gel of sufficient yield strength to resist flow from an inverted container at a concentration of 10 wt-%* or less. Employing this criterion, only acetylene black and pyrogenic silica were considered suitable for rheological studies with hydrazine and UDMH (Table 1). Of the remaining gelling agents, Gantrez and Carbopol are of interest because of their ability to gel or thicken hydrazine at low concentrations without detracting much from the energy of the system as a propellant.

*The unit used in the screening studies was wt-%, for the convenience of preparing samples. However, for the rheological studies, it was necessary to express concentration as vol-% in order to use existing equations.

Table 1
Results of Screening Tests of Gelling Agents for Use with Hydrazine and/or UDMH

Gelling Agent	Hydrazine		UDMH	
	Additive (wt-%)	Result	Additive (wt-%)	Result
Carbons				
Acetylene black	6.0	Gel	6.0	Gel
Chlorocarbon, washed	10.0	Gel	16.0	Gel
Vulcan XC 72R	10.0	Suspn. (a)	6.0	Suspn. (b)
Elftex 8	10.0	Suspn. (a)	16.0	Suspn. (c)
Sterling 10R	10.0	Suspn. (a)	11.0	Suspn. (c)
Silicas				
Cab-O-Sil	9.0	Gel (d)	6.0	Gel
K-3 Silica	18.0	Th. Liq. (e)	7.0	Gel
Santocel C		Ppt. (f)	13.8	Gel
DuPont Hyperfine Silica		Ppt.		Ppt.
GS Hydrophobic Silica		Ppt.		Ppt.
Clays				
Ben-a-gel	10.0	Suspn.		Ppt.
Bentone 27		Ppt.	8.0	W. Gel (g)
Bentone 34		Ppt.		Ppt.
Bentone 38		Ppt.	10.0	W. Gel
Attagel 20		Ppt.	17.0	Suspn.
Alumina, Modified				
Baymal		Ppt.		Ppt.
Synthetic Polymers				
Gantrez AN 169	2.0	Gel		Ppt.
Copolymer of methyl vinyl ether and maleic anhydride				
Carbopol 934	2-10	Th. Liq.		Ppt.
Carboxy vinyl polymer				
Natural Products				
CMC				
Sodium carboxy methyl cellulose	7.0	Visc. Liq.		Ppt.
Natrosol				
Hydroxy ethyl cellulose	4.0	Visc. Liq.	4.0	Visc. Liq.
Jaguar				
Guar gum		Ppt.	1.0	Ppt.
Thixatrol ST				
Hydrogenated castor oil	14.0	Gel (h)	9.0	Gel (h)
Thixcin E				
Hydrogenated castor oil	14.0	Gel (h)	11.0	Gel (h)

a. No thickening, much gas evolution but no apparent heat.
b. Thins out on standing overnight.
c. Partially settles out on standing.
d. Shear thins.
e. Th. Liq. = thickened liquid, shear thins.
f. Ppt. = precipitate forms at concentrations below 10% by wt.
g. W. Gel = weak gel -- will flow from inverted container.
h. Not necessarily minimum quantity required for gelation. Gel strength improves on standing.

Hydrogenated castor oil gels both hydrazine and UDMH, although rather large quantities of gelling agent are required. It is possible that somewhat less gelling agent than indicated in Table 1 could be used, since the strength of these gels improves on standing.

Finally, hydroxy ethyl cellulose (Natrosol) was found to be an effective thickener for both hydrazine and UDMH. Although these thickened liquids do not meet the requirements of gels, it is possible that Natrosol could be used in conjunction with another more efficient gelling agent or additive to reduce the overall amount of agent required in the system.

The tendency of suspensions of pyrogenic silica in polar liquids to break down irreversibly or fluidize when subjected to high shear is well known (3). This behavior is probably due to the fact that high shear mixing destroys the aggregates of silica particles (which give structure to the suspension) and exposes more hydroxyl groups to the suspending liquid. Since gelation depends on the proper balance between particle-particle and particle-liquid interactions, the exposure of more hydroxyl groups to the liquid increases the particle-liquid interactions at the expense of the particle-particle interactions. As a result, the silica particles become effectively solvated, and the gel structure is destroyed.

In the present study an attempt was made to improve the gelling properties of pyrogenic silica in polar liquids by chemically changing the nature of its surface hydroxyl groups. Thus, by converting some of the hydroxyl groups to methoxyl groups, it was felt that the particle-liquid interaction could be reduced to the point where gelation would occur. However, it was found that merely refluxing Cab-O-Sil with methyl alcohol in the presence of hydrochloric acid for 15 minutes so increased the particle-particle interaction that the product precipitated from both hydrazine and UDMH.

In another experiment, an attempt was made to take advantage of the fact that when pyrogenic silica is heated in a vacuum, between 200° and 400°C, adjacent surface hydroxyl groups condense by liberation of H_2O (4). These hydroxyl groups are readily reconstituted when the temperature is lowered and the sample is exposed to moisture. Since the number of hydroxyl groups so condensed is a function of temperature, it was reasoned that by heating the Cab-O-Sil in a vacuum at various temperatures between 200° and 400°C and then lowering the temperature and releasing the vacuum with methyl alcohol, a controlled number of hydroxyl groups could be converted to methoxyl groups. Thus, by reducing the number of hydroxyl groups in this manner, it was felt that the gelling properties of Cab-O-Sil in polar liquids could be changed in a regulated manner. However, it was found that heating Cab-O-Sil for six hours in a vacuum at 200°, 300°, and 375°C, then lowering the temperature and releasing the vacuum with methyl alcohol, in no way improved its gelling properties in hydrazine.

Another gelling agent, Gantrez AN 169, proved to be an excellent gelling agent for hydrazine, but not for UDMH. Since this agent has repeating anhydride groups in its structure, an attempt was made to improve its properties by forming the partial methyl and partial hexyl esters. However, the esterified products would only thicken hydrazine and precipitated from UDMH.

RHEOLOGICAL STUDIES

Acetylene Black/Hydrazine System

A series of samples containing 0.51 to 3.59 vol-% of acetylene black in hydrazine was prepared. Since the minimum gelling concentration for this system is 3.17 vol-%, this series covered the range in concentration from weak suspension to strong gel.

The flow curves for acetylene black/hydrazine suspensions, as shown in Fig. 1, are ideal at subgelling concentrations; i.e., below 3.17 vol-%, they consist of normal hysteresis loops. Notably absent from these flow curves is any indication of τ_0, the experimental yield stress, which was found in the Ben-a-gel/water system. Apparently the value of τ_0 is less than the shear stress at the lowest shear rate. At 3.17 vol-%, the area between the upcurve and downcurve is greatly reduced at lower shear rates and completely disappears above 350 sec^{-1}. This result implies that at shear rates above 350 sec^{-1}, the structure is rebuilding so rapidly that the downcurve cannot be detected. The fact that this behavior was observed in a duplicate sample and only at 3.17 vol-%, which is the minimum gelling concentration, suggests that this phenomenon might be related to the rapid buildup in structure that is associated with the transition from thixotropic liquid to gel.

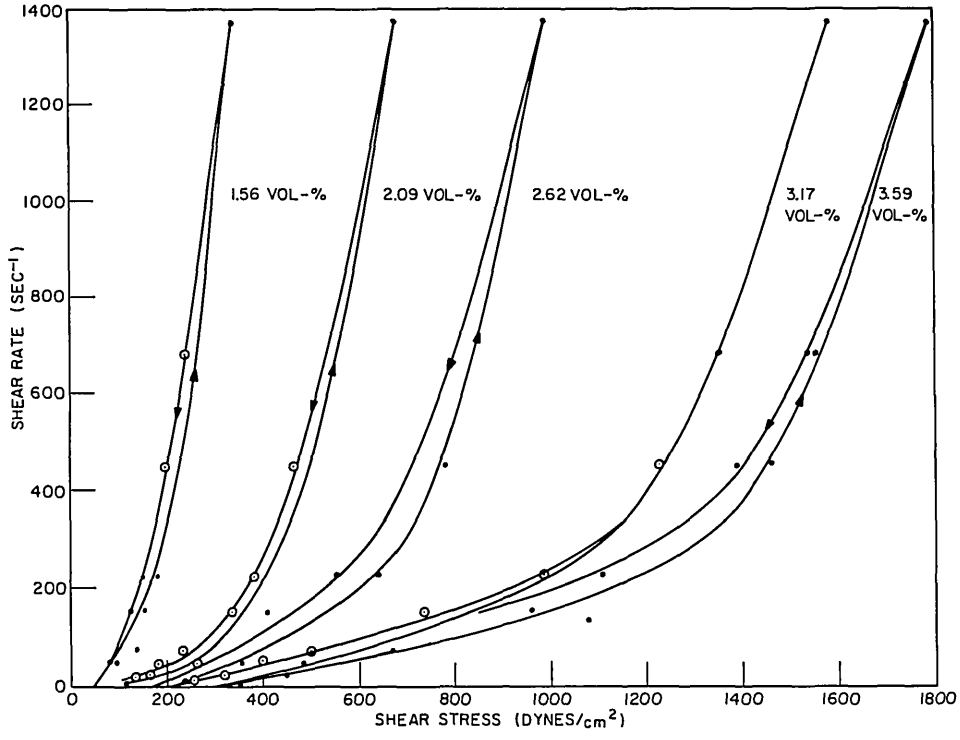

Fig. 1 - Flow curves for acetylene black/hydrazine suspensions

Also, at 3.17 vol-% and above, the flow curves tend to become more convex towards the shear stress axis, indicating that for these concentrations the initially high viscosity changes slowly with increasing shear rate, up to a value of approximately 300 sec^{-1}. Above this shear rate, the viscosity decreases much more rapidly, until the upcurve straightens out and a constant value is reached.

The plastic viscosity of the acetylene black/hydrazine suspensions is given in Fig. 2 as a function of concentration. Two samples were run at each concentration, using both the low shear and high shear cup and bob, and the average plastic viscosities at each shear rate were determined.

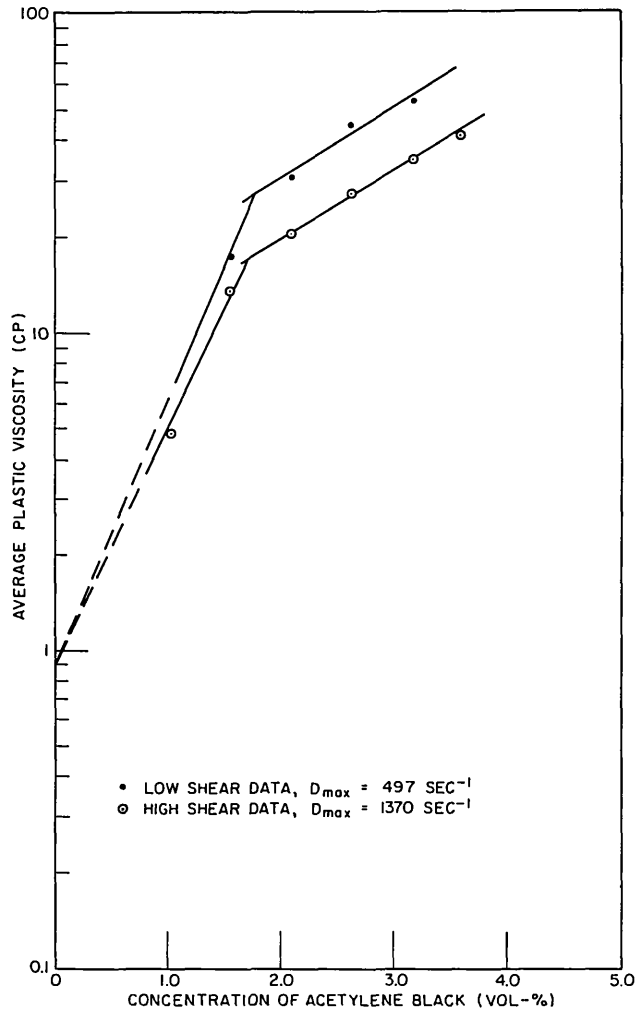

Fig. 2 - Average plastic viscosity of acetylene black/hydrazine suspensions as a function of concentration

According to these curves, the plastic viscosity of acetylene black/hydrazine suspensions follows the same two experimental laws (Eqs. 2 and 3) as aqueous suspensions of Ben-a-gel (2). However, in the case of the acetylene black/hydrazine system, the break in the curve marking the transition from one exponential law to the other did not coincide with transition from thixotropic liquid to gel as it did for the Ben-a-gel/water system. Instead, in Fig. 2, the break occurs at 1.7 vol-%, which is below the minimum gelling concentration for acetylene black in hydrazine.

Moreover, when τ_{ext} and τ_B are plotted as a function of concentration for the acetylene black/hydrazine system (Figs. 3 and 4), the break in the curve is not as sharply defined as it was for the Ben-a-gel/water system. For the acetylene black/hydrazine system, the break occurs over the range of 1.7-2.0 vol-%, with the higher values being found for the low shear cup and bob. This behavior may reflect more on the accuracy of the measurement than on a characteristic of the sample, since the accuracy of the instrument falls off at lower values.

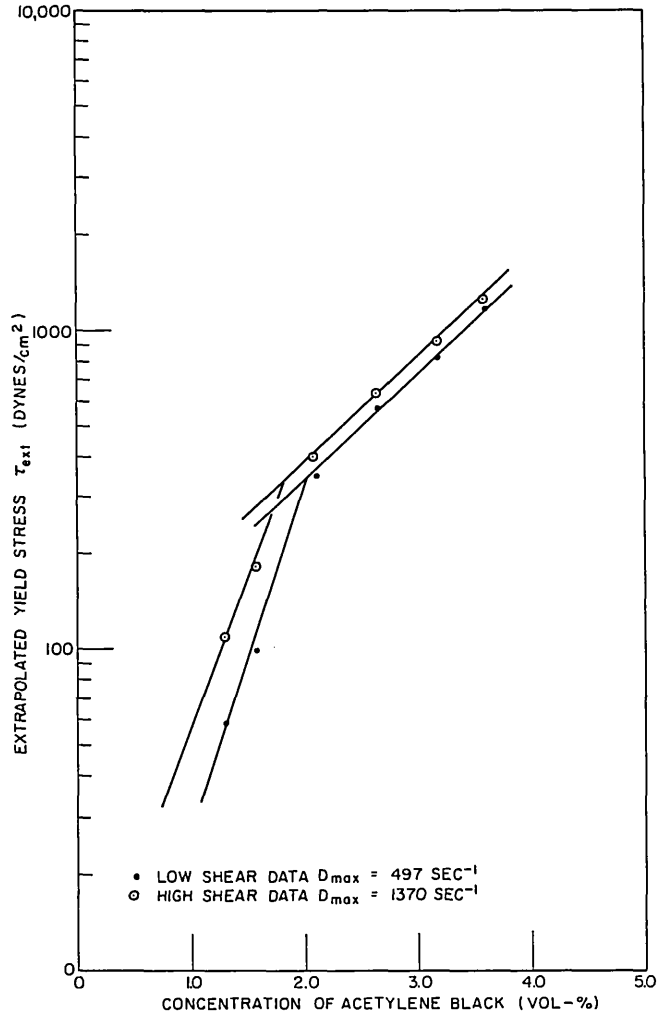

Fig. 3 - Average extrapolated yield-stress values for acetylene black/hydrazine suspensions as a function of concentration

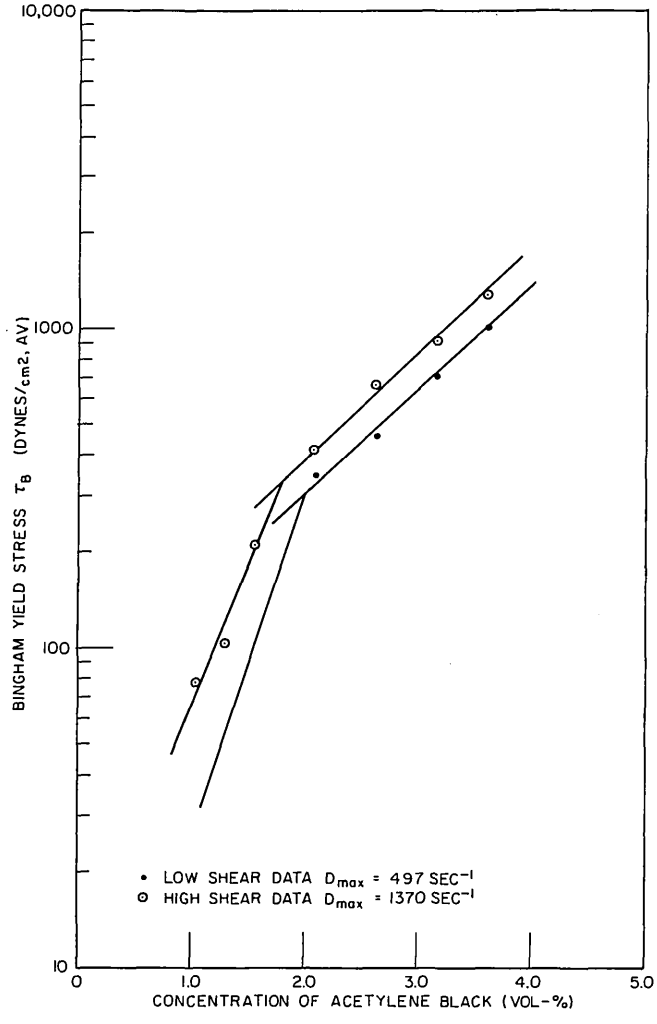

Fig. 4 - Average Bingham yield stress for acetylene black/hydrazine suspensions as a function of concentration

The fact that the break in the curve for the acetylene black/hydrazine system does not coincide with the change from thixotropic liquid to gel does not detract from the significance of this transition point. In this case, the break may mark the concentration at which a three-dimensional structure is reached. If this is true, then the particle-particle forces apparently are not sufficiently developed at the transition point to prevent the suspension from flowing from the inverted container, and hence the suspension is still regarded as a liquid for the purposes of this discussion.

Another feature of the acetylene black/hydrazine system is that the values for the yield stresses, τ_B and τ_{ext}, appear to be dependent upon shear, rate with lower values being obtained at the lower shear rate. For the Ben-a-gel/water system, the yield stress values were independent of shear rate.

The lower values for $\tau_{ext.}$ at lower shear rates are in accord with the findings of Weltmann and Green (5). No physical significance is attached to this observation; it merely means that the downcurves for the acetylene black/hydrazine system do not converge at a single point on the shear-rate axis as they do for the Ben-a-gel/water system.

That lower values for τ_B are found at lower shear rates indicates that the upcurves have not straightened out over the shear-rate range covered by the low shear cup and bob. Only when the upcurve assumes straight-line character well below 497 sec^{-1} (which is D_{max} for the low shear cup and bob) will the values for τ_B be independent of shear rate.

The fact that both τ_B and τ_{ext} are dependent upon shear rate means that neither of these terms can be used by itself for specifying the requirements of a gelled propellant system involving acetylene black and hydrazine. It would be necessary to specify the yield point at a particular shear rate in order to describe these systems fully.

Inasmuch as the acetylene black/hydrazine system displays normal, reproducible hysteresis loops, and since the plastic viscosity and yield stresses can be related exponentially to concentration, this system may be regarded as an ideal thixotropic gel system.

Pyrogenic Silica/n-Decane System

Pyrogenic silica was obtained in a range of particle sizes from two sources in order to establish the effect of particle size on gelling ability. The specifications of these silicas are given in Table 2. Since both silicas are prepared by the same process (vapor-phase hydrolysis of $SiCl_4$ at 1100°C), the purity is consistent. Aerosil TT600 has a higher moisture content after heating to 105°C, indicating that it has a greater proportion of surface hydroxyl groups than the other samples. The individual silicas differ then not only in particle size but also in the percentage of the surface covered with hydroxyl groups.

Since the gelling efficiency of pyrogenic silica increases with decreasing polarity of the suspending liquid, a study was made using n-decane as a representative nonpolar liquid to determine if ideal gels would be formed with this system. For this purpose, flow curves were prepared for a series of samples containing from 0.92 to 2.82 vol-% of both Aerosil and Cab-O-Sil in n-decane. This concentration range covers the thixotropic liquid-to-gel region. The resulting flow curves were not smooth hysteresis loops, such as were found for the Ben-a-gel/water system (2). Instead the flow curves for the Aerosil/n-decane system revealed that plug-flow or slip-flow occurs in all samples containing 1.39 vol-% or greater of silica, and there is even some evidence of it at lower concentrations.

This type of flow behavior can best be illustrated by considering a typical recorder tracing (Fig. 5) of the shear-stress values obtained when an Aerosil/n-decane suspension is sheared in the viscometer using the hysteresis loop method. The numbers under the

Table 2
Analysis and Properties of Pyrogenic Silicas

Analysis and Properties	Cab-O-Sil (a)		Aerosil (b)			
	M-5	H-5	2491/460	2491/380	TT 600	Type O
SiO_2 (%)	99.9	99.0	>99.8 (c)	>99.8 (c)	>99.8 (c)	>99.8 (c)
Particle size from BET Area (mμ)	13.6	8.4	5.9	7.2	13.6	15.5
Moisture, after heating to 105°C (%)	<1.5	<1.5	<1.5	<1.5	<2.5	<1.5
HCl (%)	n.a. (d)	n.a.	<0.025	<0.025	<0.025	<0.025
Al_2O_3 (%)	n.a.	n.a.	<0.05	<0.05	<0.05	<0.03
TiO_2 (%)	n.a.	n.a.	<0.003	<0.003	<0.003	<0.001
Grit (%)	n.a.	n.a.	<0.05	<0.05	<0.05	<0.03
pH (4% aqueous suspension)	3.6-4.2	n.a.	3.6-4.3	3.6-4.3	3.6-4.3	3.6-4.3

a. Godfrey L. Cabot, Inc., Boston, Massachusetts.
b. Degussa, Frankfurt, Germany.
c. Moisture-free basis.
d. Not available.

steps refer to the shear rate, which is increased from 3 to 497 sec^{-1} to form the upcurve portion of the flow curve, and then decreased to 3 sec^{-1} to form the downcurve. The flow curve prepared from this recorder tracing is shown in Fig. 6.

As indicated in Figs. 5 and 6, when an Aerosil/n-decane suspension is placed in a cup and bob type viscometer and the instrument shifted to its lowest shear rate, there is no movement of the bob until a certain yield stress, τ_0, is overcome. Then there is a sharp drop in the recorded shear stress as the bob begins to rotate. As the shear rate is increased to 18 sec^{-1}, the shear-stress values increase in a normal, step-wise fashion, just as was found for the Ben-a-gel/water system. However, when the shear rate is increased from 18 to 28 sec^{-1}, there is a sharp rise in the recorded shear stress as indicated in both figures.

What is taking place in the annulus may be described as follows. After the initial yield stress, τ_0, is overcome, the material starts to flow where the stress is the largest. In a rotating-bob viscometer, the shear stress is greatest at the surface of the bob as indicated by Eq. (5) (6a).

$$\tau = \frac{T}{2\pi hr^2} \tag{5}$$

where

τ = shear stress (dynes/cm^2)

T = torque (dyne-cm)

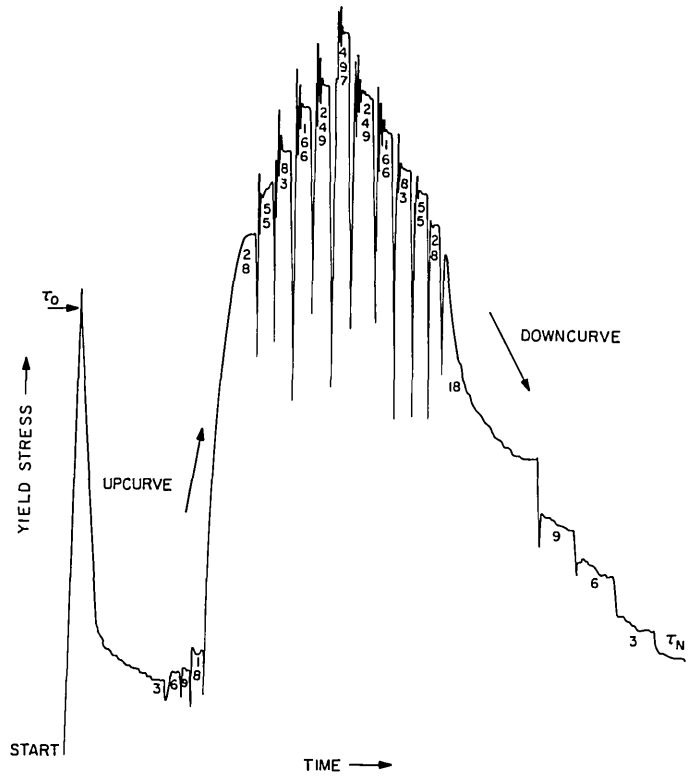

Fig. 5 - Recorder tracing of shear stresses obtained during preparation of flow curve, sample: 1.39 vol-% of Aerosil-460 in n-decane, low shear data (numbers under the curve refer to shear rate)

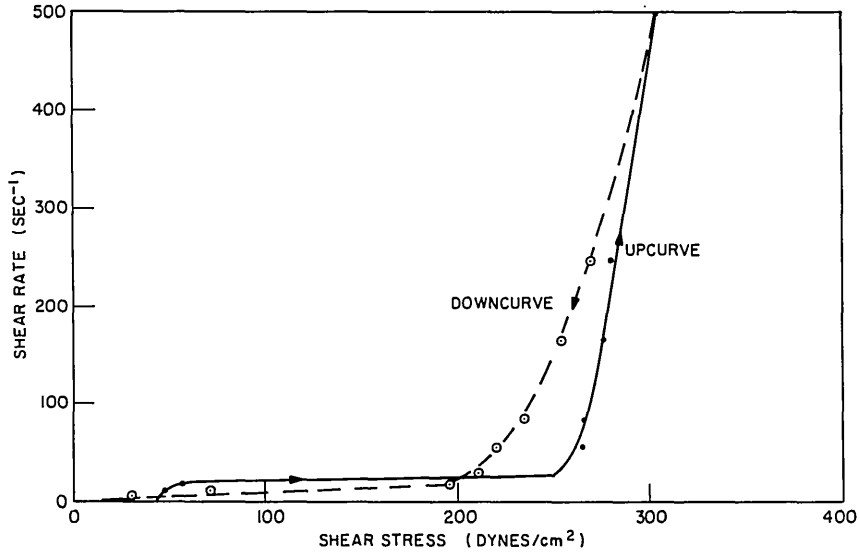

Fig. 6 - Flow curve for a suspension of 1.39 vol-% of Aerosil-460 in n-decane

h = depth of immersion of bob (cm)

r = radius of cup or bob.

Thus, when r = radius of the cup, τ = the shear stress at the surface of the cup.

Since the radius of the cup is greater than that of the bob, at low shear rates, only the material closest to the bob is sheared. This is because at low shear rates, the only place in the annulus where the shear stress is sufficient to initiate flow is at the surface of the bob. It is only when the shear stress at the surface of the cup equals τ_0 that all of the material in the annulus will flow. According to Fig. 5, this event occurs when the shear rate is increased to 27 sec^{-1}. Since at this speed the bob is rotating fast enough that the entire sample is being sheared, the transition is made from plug to laminar flow.

On the downcurve, the reverse takes place. When the shear stress at the surface of the cup falls below the yield stress, the material begins to set up at the surface of the cup, and consequently only the material closest to the bob is sheared at low shear rates. In Fig. 5 this appears to take place when the shear rate reaches 18 sec^{-1}.

Since with the Rotovisco, the shear rate is increased in a step-wise fashion, it is impossible to state the exact shear rate at which plug flow ends. Only the range in shear rate during which the transition from plug to laminar flow occurs can be determined. These ranges for both the low shear and high shear cup and bob arrangements are shown in Fig. 7. Since the shear-rate ranges for both the MVI and MVIIP cup and bob arrangements overlap, it is possible to narrow down the range where plug flow ends. Thus, in Fig. 7, the hatched area represents the region where the shear-rate ranges overlap and consequently the range where plug flow ends for all samples at a given concentration.

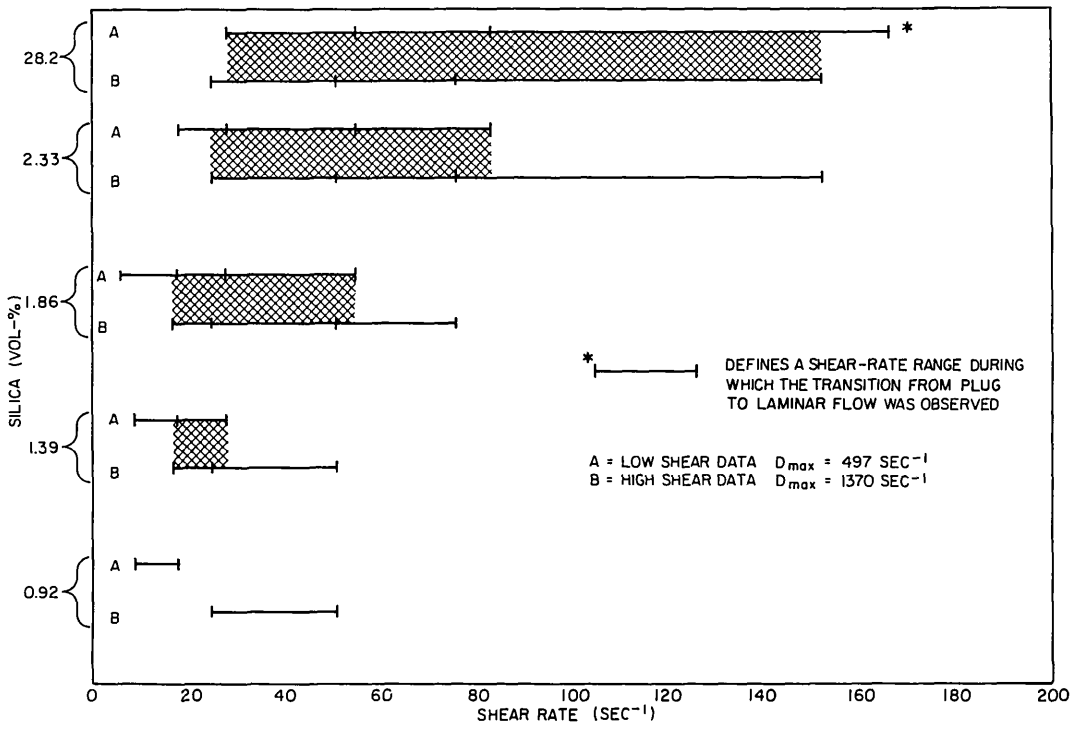

Fig. 7 - Range in shear rate where transition from plug to laminar flow occurs for Aerosil/n-decane suspensions

From this figure it can be seen that the transition from plug to laminar flow occurs at higher shear rates as the concentration of silica increases. This means that as the concentration of silica is increased, higher shear rates must be employed before all of the sample in the annulus will be sheared.

In addition to displaying plug flow, the rheograms for the Aerosil and Cab-O-Sil/n-decane suspensions were not found to be very reproducible at higher concentrations, i.e., at 2.3 vol-% of silica or greater. At this concentration, all of the suspensions set up as gels during their preparation after shearing for 30 sec or less. Under these conditions, it is difficult to obtain uniform dispersions, and hence reproducible flow curves. Occasionally a sample was encountered that had not been completely sheared during preparation, and hence had not developed maximum properties. The flowcurve for such a sample would indicate that structure was being built up in the sample during the course of running the upcurve, since the downcurve would lie to the right of the upcurve. The data from such a flowcurve were discarded as unreliable.

However, the majority of the flowcurves for the silica/n-decane suspensions were normal, and from these curves the data for the plastic viscosity and the various yield stresses were obtained. In Fig. 8, the plastic viscosity for the Aerosil suspensions are plotted as a function of concentration. These data were obtained with the low shear cup

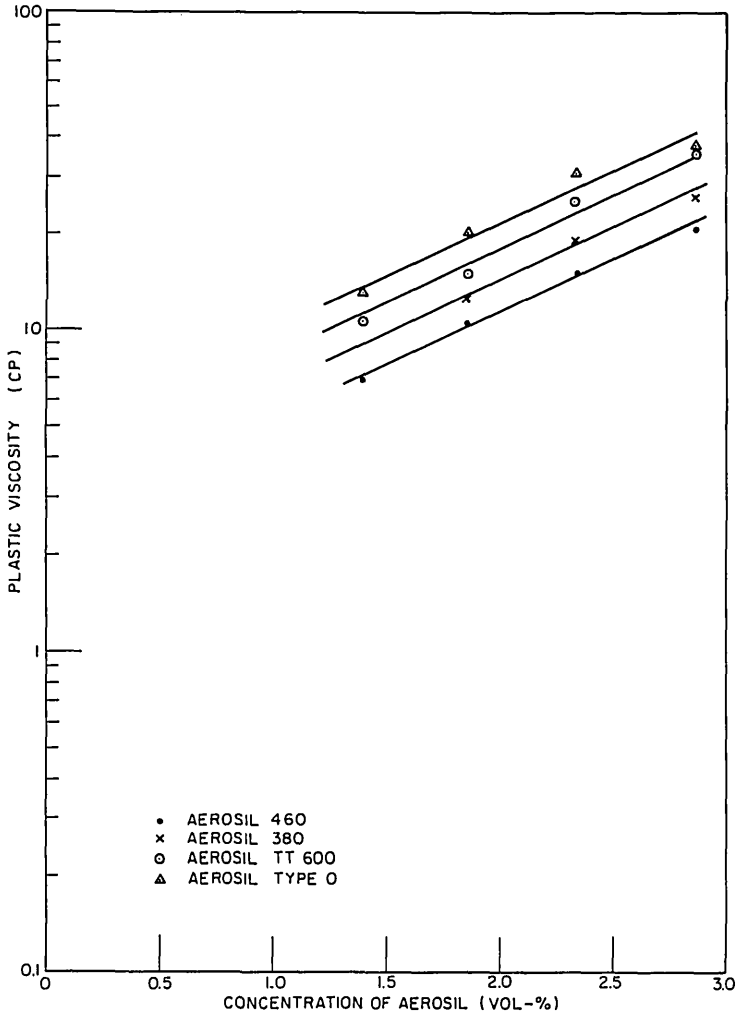

Fig. 8 - Plastic viscosity of Aerosil/n-decane suspensions as a function of concentration, low shear data, D_{max} = 497 sec^{-1}

and bob arrangement, and hence the viscosities at lower concentrations could not be reliably ascertained. However, these curves do show that at higher concentrations, Weltmann and Green's law (Eq. 3) is followed.

In Fig. 9, the data obtained at high shear are given. The data points for the Aerosil 380 dispersions are not included in this figure, since they lie too close to the corresponding points for Aerosil 460. As shown in the figure, it was possible to get viscosity data at lower concentrations (0.92 vol-%) with the high shear cup and bob. These data show the location of the break in the curve and hence the transition from Weltmann and Green's equation to Arrhenius' law.

As in the case with the acetylene black/hydrazine suspensions, the break in the curve did not coincide with the transition from thixotropic liquid to gel, but rather occurred at some subgelling concentration. With the Aerosil/n-decane system, a gel did not form until the concentration reached 2.3 vol-%, whereas the break in the curve occurred at 1.4 vol-% (Fig. 9). However, for both systems, the operation of two exponential laws relating plastic viscosity to concentration is clearly in evidence.

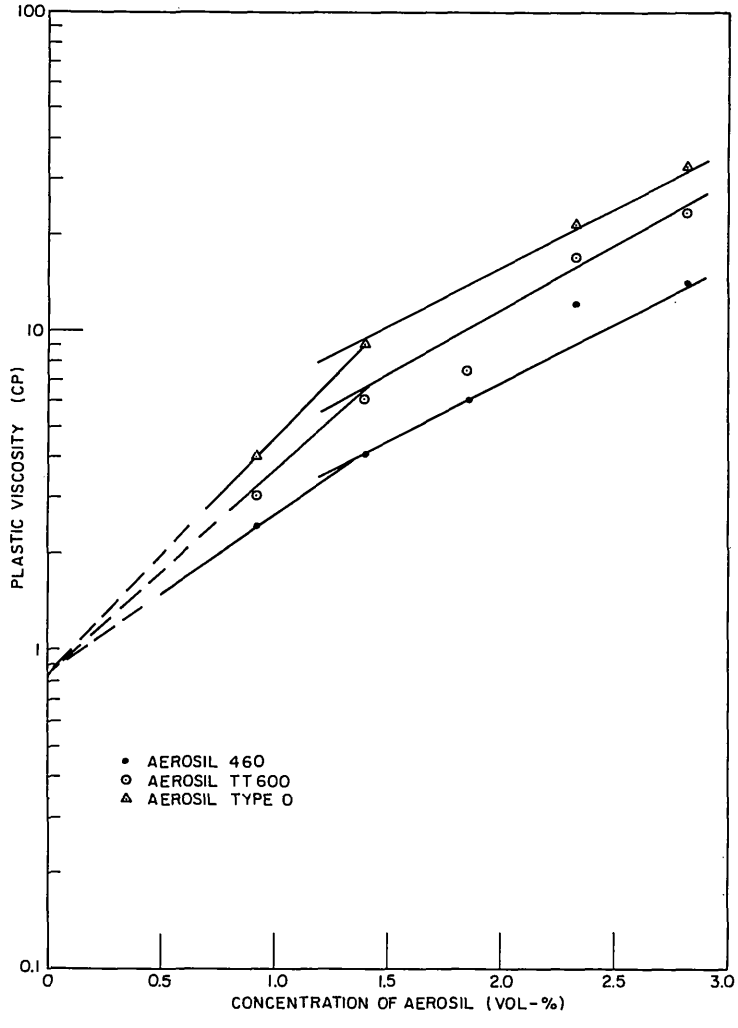

Fig. 9 - Plastic viscosity of Aerosil/n-decane suspensions as a function of concentration, high shear data, D_{max} = 1370 sec^{-1}

The data for the Cab-O-Sil/n-decane suspensions are given in Fig. 10. In general, these suspensions were found to give poorer quality flow curves than Aerosil suspensions. Also, the plastic viscosities of the Cab-O-Sil suspensions were found to be greater than those of Aerosil suspensions of the same particle size. The cause of this discrepancy was not determined. However, this effect is not due to absorbed moisture, since drying of the silica at 125°C did not change this relationship. Furthermore, according to Fig. 10, the Cab-O-Sil suspensions do not show a break in the curve, as was found for the Aerosil suspensions. It is felt that such a break probably occurs at low concentrations but, due to the limitations of the viscometer, it could not be detected in this study.

The values for the various yield points, τ_0, τ_B, and τ_{ext} for the various silica suspensions were also determined. In Fig. 11, the τ_{ext} values for Aerosil/n-decane suspensions are plotted as a function of concentration. Although the reproducibility of these and the other yield-stress values is far from satisfactory, they do appear to follow the same exponential law as was found for the Ben-a-gel/water system (2). The curves for τ_B and τ_0 are not shown, since the precision of the data is no better than that shown in Fig. 10.

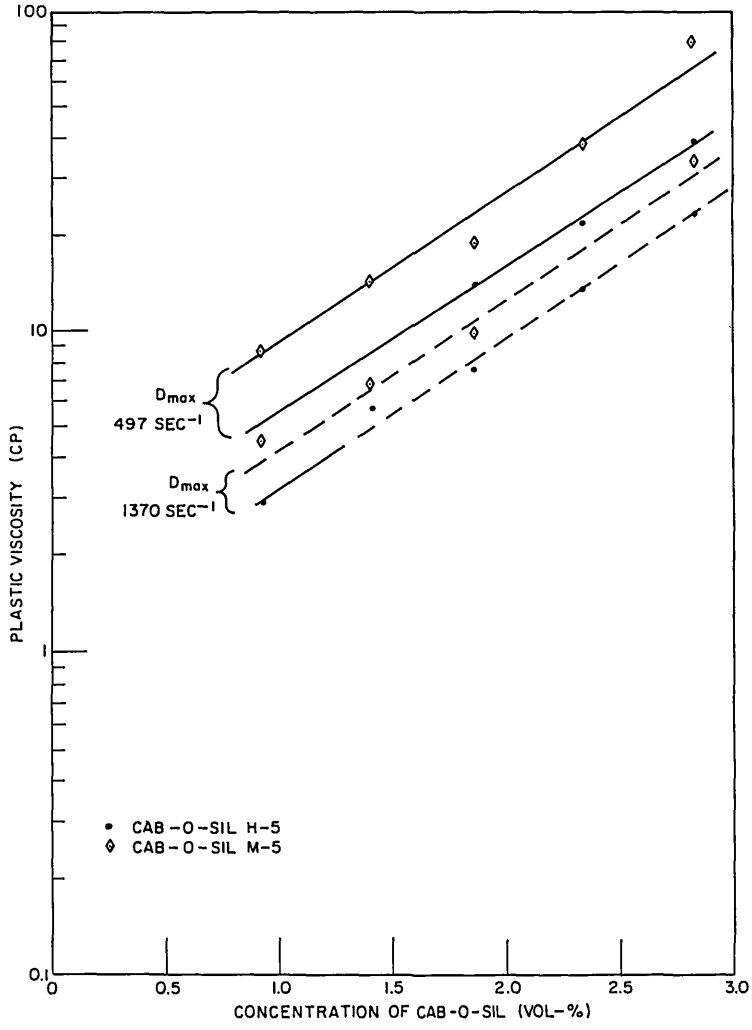

Fig. 10 - Plastic viscosity of Cab-O-Sil M-5/ and H-5/n-decane suspensions as a function of concentration

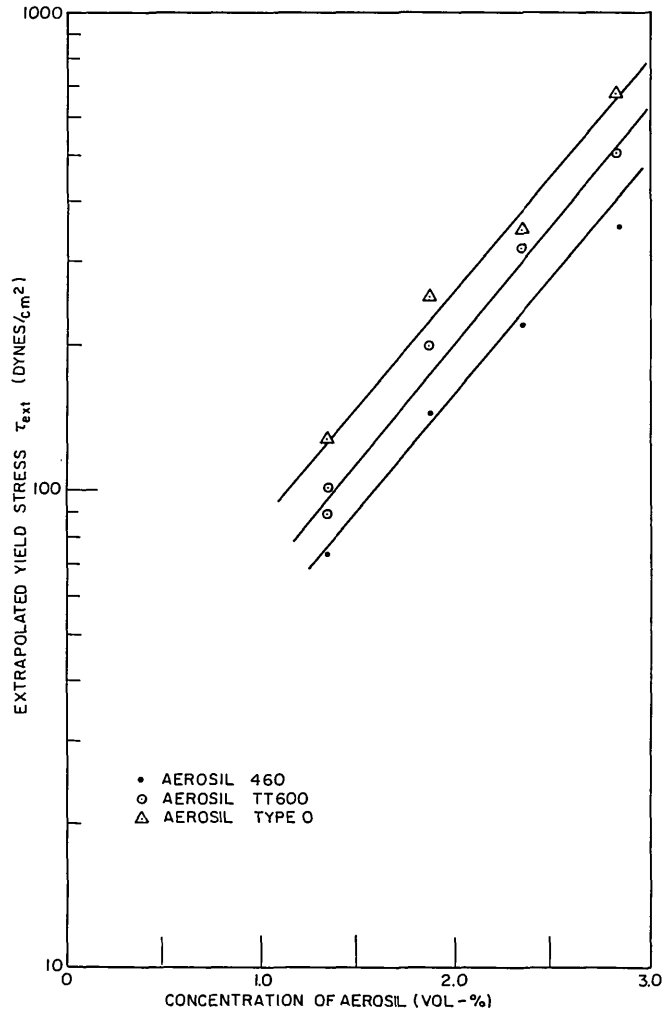

Fig. 11 - Extrapolated yield-stress values for Aerosil/n-decane suspensions as a function of concentration, high shear data, $D_{max} = 1370\ sec^{-1}$

The effect of particle size of the silica on plastic viscosity of Aerosil/n-decane suspensions was also investigated. The results of this study, as presented in Fig. 12, show that at a fixed concentration of Aerosil, plastic viscosity increases logarithmically with particle size, the increase amounting to 70 to 85 percent over the particle-size range studied.

The data for the Cab-O-Sil/n-decane suspensions are not shown in Fig. 12 due to the poor reproducibility of the results. However, at a given concentration of gelling agent, the Cab-O-Sil suspensions showed higher viscosities than the Aerosil suspensions of the same particle size. This increased performance of Cab-O-Sil suggests that perhaps the Cab-O-Sil particles had a greater proportion of surface hydroxyl groups than the Aerosil particles, thereby making Cab-O-Sil a more effective gelling agent in less polar liquids.

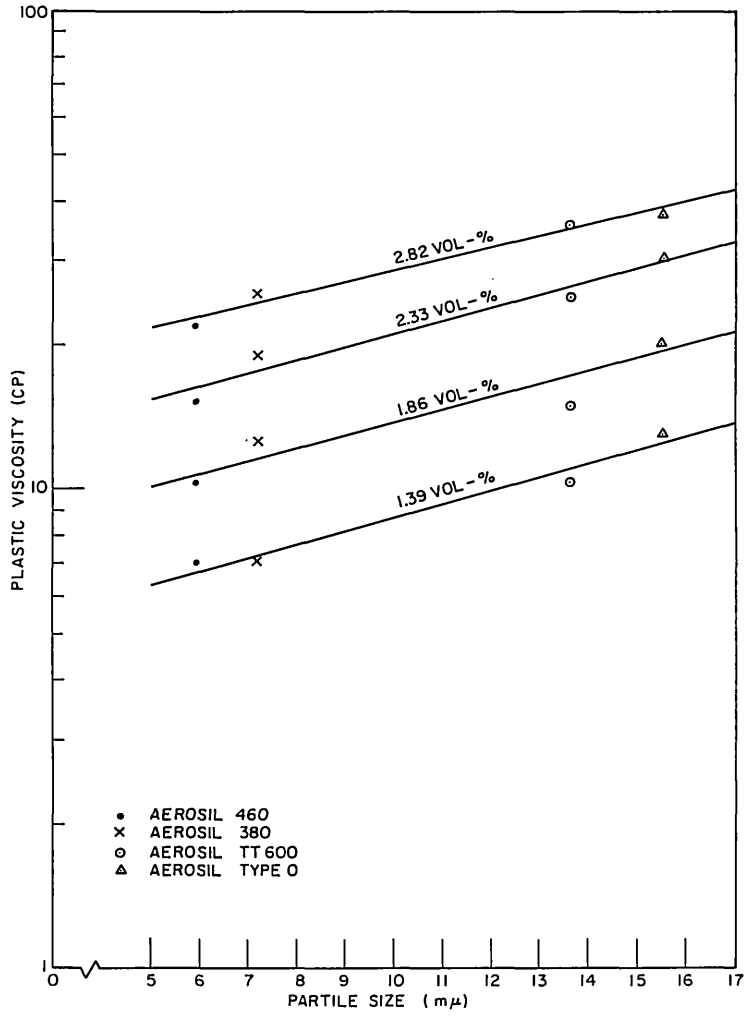

Fig. 12 - Effect of particle size on the average plastic viscosity of Aerosil/n-decane suspensions, low shear data, D_{max} = 497 sec^{-1}

Pyrogenic Silica in Polar Liquids

The rheology of the pyrogenic silica in polar liquids was also investigated, since it was expected that such liquids would more closely resemble hydrazine and UDMH in behavior. For this purpose, suspensions of Aerosil in water and of Aerosil and Cab-O-Sil in n-propyl and isopropyl alcohols were prepared. Since these suspensions are not stable gels (their structure is completely and irreversibly* broken down with high-speed shearing), satisfactory flow curves were not obtained. As a result, the thickening power of the individual silicas in a particular system had to be evaluated on the basis of the

*The structures do not rebuild themselves during the life time of the experiment. Several days or weeks are required before the gels will be restored.

apparent viscosity of the suspension after the upcurve had been traced. The apparent viscosity* is defined as the ratio of the shear stress to the shear rate.

In Fig. 13, the thickening efficiency of Aerosil in aqueous suspension is given as a function of particle size. The apparent viscosity is highest when the particle size is 7.2 mμ, but the differences involved are rather small. The smaller particle size Cab-O-Sil, H-5, was also found to be a better thickening agent in aqueous suspension than the M-5.

The thickening power of Aerosil and Cab-O-Sil in n-propyl and isopropyl alcohols is shown in Fig. 14. As in aqueous suspensions, the apparent viscosity is highest at 7.2 mμ; only the effect is more pronounced in the alcoholic suspensions. The data points for Cab-O-Sil do not lie on the Aerosil curves, but they do indicate that the thickening efficiency of pyrogenic silica in n-propyl and isopropyl alcohols is greater for the smaller particle size material.

Suspensions of Aerosil and Cab-O-Sil in hydrazine were found to resemble the aqueous and alcoholic suspensions in their tendency to break down irreversibly with shear. Also, since these suspensions did not always give normal flow curves, apparent viscosities were used to compare the effectiveness of the various silicas in hydrazine. The results of these studies, as shown in Fig. 15, show that the thickening efficiency of pyrogenic silica is highest at a particle size of 13.6 mμ. Again, the data points for Cab-O-Sil dispersions do not fit the curve for the Aerosil suspensions, but they do show a similar behavior.

Flow curves for suspensions of Aerosil and Cab-O-Sil in UDMH were not always normal, particularly at higher concentrations, despite the fact that both of these silicas formed good gels at concentrations of 1.8 to 2.2 vol-%. However, this behavior was not entirely unexpected, since normal flow curves were not encountered at higher concentrations in the simpler Aerosil/n-decane system. The abnormalities in the flow curves included plug-flow and an indication of structural buildup which was characterized by a rather sharp increase in shear stress when the sample is sheared at the maximum shear rate.

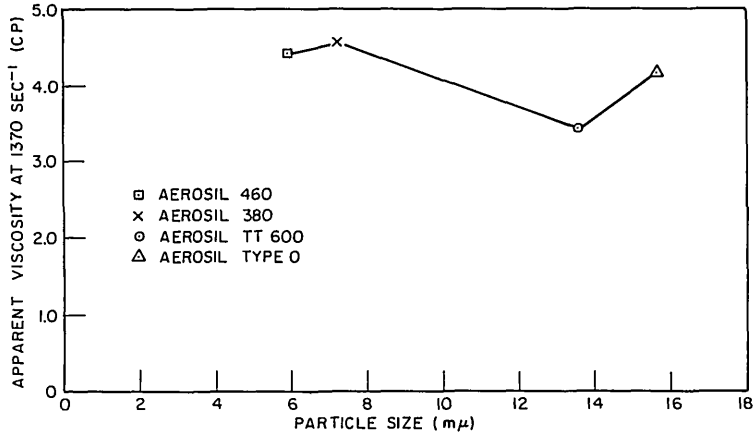

Fig. 13 - Effect of particle size on apparent viscosity of suspensions of Aerosil in water, concentration of silica 2.3 vol-%

*The concept of apparent viscosity involves inherent contradiction (6b), since it implies that the suspension behaves as a Newtonian liquid. The term is used here since, in the absence of a reliable downcurve, it is the only available measurement on the system.

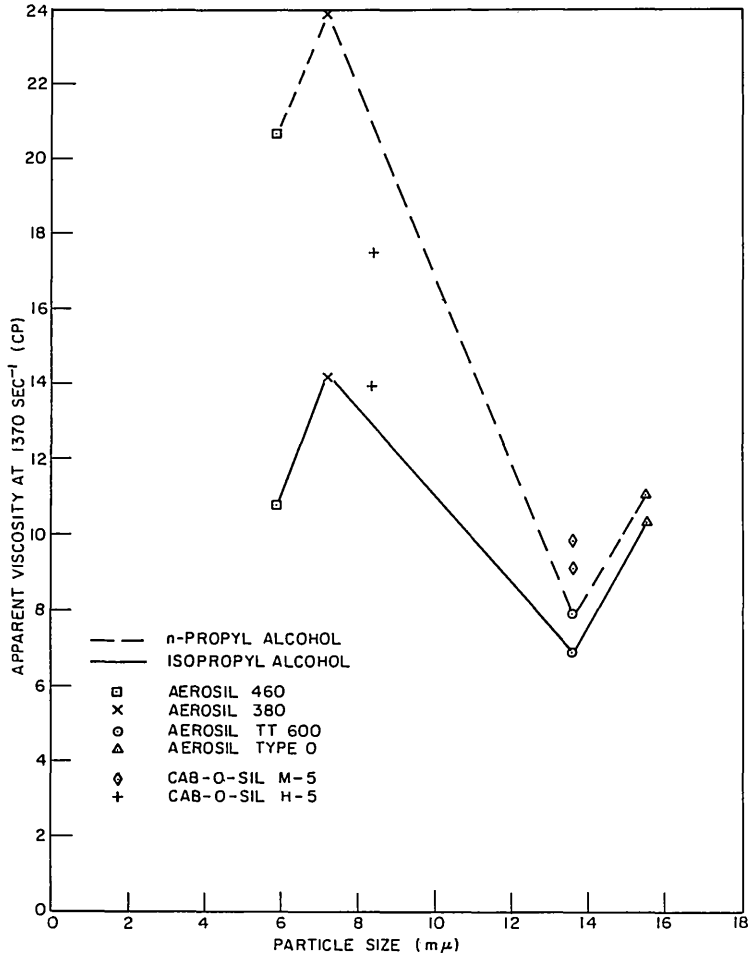

Fig. 14 - Effect of particle size on apparent viscosity of suspensions of Aerosil and Cab-O-Sil in n-propyl and isopropyl alcohols, concentration of silica 3.8 vol-%

In the absence of normal flowcurves, apparent viscosities were used to compare the thickening efficiency of pyrogenic silica in UDMH. The results are given in Fig. 16. The curves for the Aerosil/UDMH suspensions resemble those obtained for the Aerosil/n-decane suspensions (Fig. 12), in that the thickening efficiency increases with increasing particle size. The data for the Cab-O-Sil/UDMH suspensions were somewhat erratic but did show the same increase in thickening efficiency with increasing particle size.

A plot of the log plastic viscosity versus vol-% of Aerosil in UDMH shows a break in the curve corresponding to about 1.3 vol-% of Aerosil, but, as in the case of the Aerosil/n-decane and of the acetylene black/hydrazine suspensions, this point did not coincide with the transition from liquid to gel. Due to the poor quality of some of the flow curves, the Aerosil/UDMH plastic-viscosity data were not sufficiently accurate to warrant reproduction.

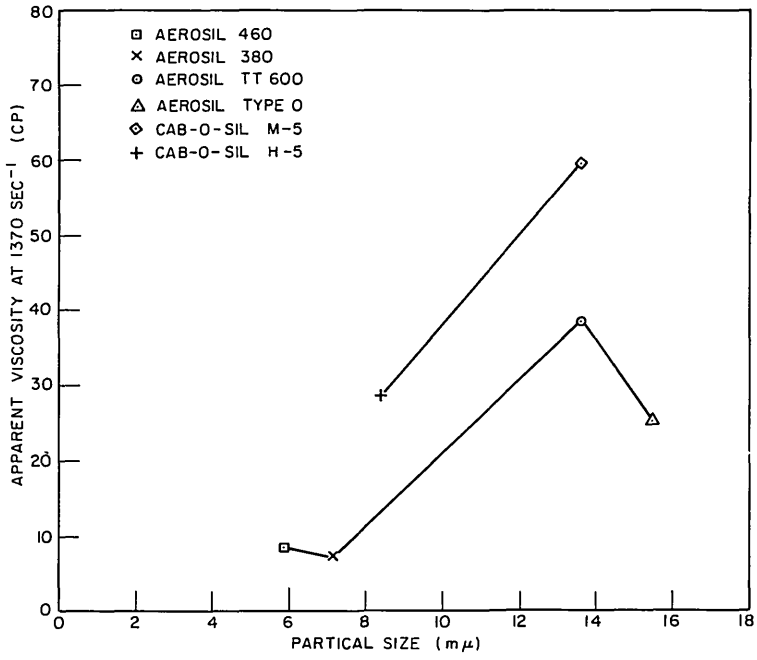

Fig. 15 - Effect of particle size on apparent viscosity of suspensions of Aerosil and Cab-O-Sil in hydrazine, concentration of silica 4.8 vol-%

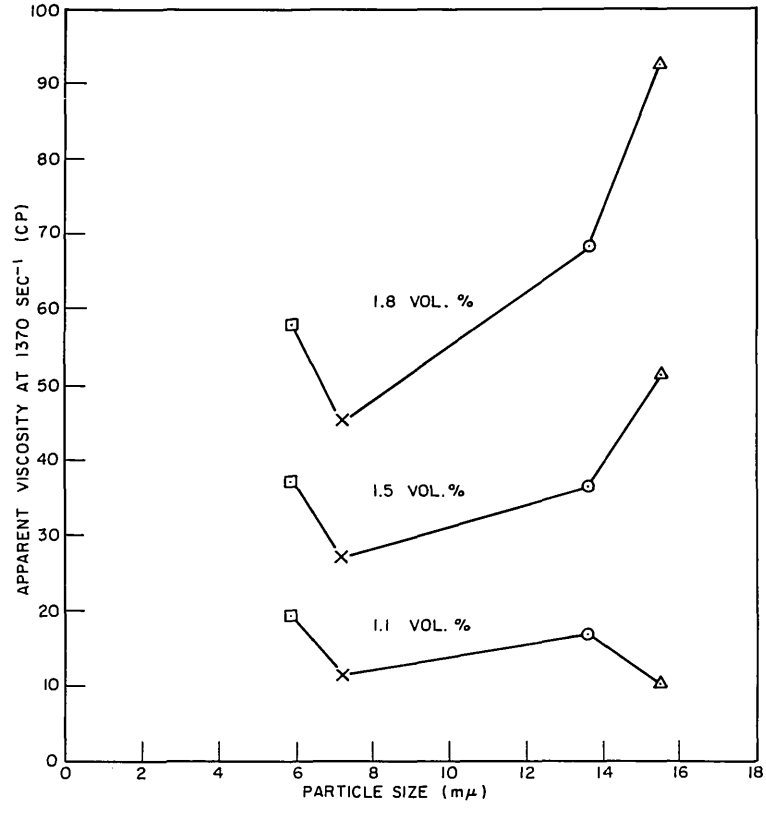

Fig. 16 - Effect of particle size on apparent viscosity of suspensions of Aerosil in UDMH

SUMMARY AND CONCLUSIONS

Of the potential gelling agents screened in this survey, only acetylene black and pyrogenic silica were selected for rheological studies with hydrazine and UDMH. Two natural products, Thixatrol ST and Thixcin E, which form gels with both hydrazine and UDMH in the 10 to 15 wt-% range, and a polymeric material, Gantrez AN-169, which gels hydrazine at 1.5 wt-% but not UDMH, were considered worthy of further study, since they are combustible additives, but are not covered in this report.

Previous studies on an ideal thixotropic system, namely Ben-a-gel in water, using the hysteresis-loop method, indicated that the flow properties of such a system could be described by either of two exponential laws, depending on concentration of gelling agent. In the present study an attempt was made to determine if gelled propellant systems followed the same laws. It was found that the acetylene black/hydrazine system behaved as an ideal system, in that its plastic viscosity and shear stress values followed Arrhenius' law at low concentrations and Weltmann and Green's equation at higher concentrations. Unlike the Ben-a-gel/water system, the break in the curve marking the transition from one exponential law to the other did not coincide with the change in behavior from thixotropic liquid to gel. Instead, it occurred at a subgelling concentration.

The other gelling agent evaluated in this study was pyrogenic silica. A preliminary investigation of this agent under "ideal" conditions, i.e., dispersed in a nonpolar liquid (n-decane), indicated that these suspensions also followed the same exponential laws, although the data at low concentrations were incomplete. However, the flow curves also exhibited plug-flow and were not very reproducible at higher concentrations.

It was also demonstrated that the thickening efficiency of pyrogenic silica in n-decane increases with particle size over the range of 5.9 to 15.5 mμ. Of the two brands of silica used in this study, Cab-O-Sil appeared to give better performance at a given concentration than the Aerosil product of the same particle size. Since the properties of these silicas are almost identical, the difference in performance may lie in a difference in the number of hydroxyl groups on the surface of the individual silicas.

The behavior of pyrogenic silica was found to be strongly dependent on the polarity of the suspending liquid or, perhaps more specifically, on the hydrogen-bonding tendency of the liquid. In water and in n-propyl and isopropyl alcohols, suspensions of pyrogenic silica were completely broken down by high shear mixing. As a result, normal flow curves were not obtained and the performance of the silica had to be evaluated on the basis of the apparent viscosity. A comparison of the apparent viscosity of the various silicas in aqueous and alcoholic suspensions revealed that in these liquids, the thickening efficiency of the silica is highest at a particle size of 7.2 mμ, as opposed to the gradual increase in performance with particle size that takes place in nonpolar liquids.

Suspensions of pyrogenic silica in hydrazine were susceptible to the same type of breakdown with shear as was found in the other polar liquids. Attempts to modify performance of this silica in hydrazine by thermal treatment followed by partial depolarization of the surface by methylation were not successful. It was found, however, that the thickening efficiency of pyrogenic silica in hydrazine is highest at a particle size of 13.6 mμ, and in this regard the performance of these suspensions resembled the pyrogenic silica/n-decane systems where maximum performance was attained with the largest particle size silica.

The behavior of pyrogenic silica in UDMH was found to be satisfactory from the standpoint of a gelling agent, but not as far as the preparation of flow curves is concerned. As a result, a smooth relationship between plastic viscosity and concentration of silica was not obtained, although a break in the curve was in evidence. Due to the nature of these data, it was not possible to demonstrate that the two exponential laws

could be applied to this system, although there were strong indications that this may be the case. Consequently, only the relationship between apparent viscosity and particle size could be worked out, and these data showed that, as in the case of n-decane suspensions, maximum performance was achieved with the largest particle size silica.

The results of the present investigation indicate that the hysteresis loop method is an effective means of studying ideal gel systems. Such systems may be defined as those which produce smooth flow curves with a hysteresis loop being formed by plotting the upcurve and downcurve. Of the gelled propellant systems covered in this study, only the acetylene black/hydrazine system gave normal flowcurves. Consequently, the hysteresis loop method is of somewhat limited value in studying practical gelled propellant systems.

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13. ABSTRACT

The hysteresis loop method was used to study the flow properties of suspensions of acetylene black in hydrazine and of pyrogenic silica in n-decane, hydrazine, unsymmetrical dimethylhydrazine, n-propyl and isopropyl alcohols, and water. It was found that the acetylene black/hydrazine system behaved ideally, in that the plastic viscosity and yield stress values of these suspensions followed Arrhenius' law at low concentrations and Weltman and Green's equation at higher concentrations.

Of the silica suspensions tested, only the pyrogenic silica/n-decane system exhibited the same exponential dependence of plastic viscosity and yield stress on concentration as was found for the ideal thixotropic suspensions. The remaining silica suspensions either broke down irreversibly under high shear conditions or were otherwise unsuitable for study by the hysteresis loop method.

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