

# A Rheological Study of the Aging of Veegum Suspensions

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Veegum HV and Veegum F suspensions, 2 per cent by weight in water, were found to be pseudoplastic at all ages for all temperatures of preparation and storage. The study is reported over the time range of a few hours to several months for temperatures from 6 to 88°. The logarithm of the apparent viscosity at any shear rate was found to be a linear function of the logarithm of time, and also to be a function of the reciprocal of temperature, obeying an Arrhenius type relation. The apparent activation energy for Veegum hydration was found to be 8000 calories per mole. A general equation is empirically derived to relate viscosity at any given shear rate with the temperature of storage and the age of the suspension.

TODAY VEEGUM<sup>1</sup> has become one of the more commonly used clay-type suspending agents for the whole range of pharmaceutical and cosmetic formulation. Probably the most popular is Veegum HV but a processed variant, Veegum F, has also a wide acceptability in certain special applications. Veegum is a complex magnesium aluminum silicate containing small amounts of other metal oxides. In composition it is intermediate between aluminum silicate (montmorillonite or bentonite) and magnesium silicate (saponite); these are platy and rod-like, respectively (1). The Veegum lattice tends to the rod form but is alleged to be the form most readily swollen by water. The extensive literature on application of this colloid as a thickening, suspending, or stabilizing agent in diverse products for human use, both internal and external, has been summarized elsewhere (2).

Veegum hydrates more completely as temperature is elevated and held during the suspension period. This hydration leads to the growth of a strong gel, the gel strength increasing with the increased temperature used to make it. Presumably this is due to the particles tending to disperse down to their ultimate structure as water penetrates and swells the lattice. Eventually the medium is a semicontinuous silicate-water complex.

Only limited literature (1, 3, 4) discusses the properties of Veegum suspensions in water alone. The temperature used to make the gel affects the resultant properties (2). The time of hydration for a given procedure as well as the method of mixing have been shown to be critical to the properties of the resultant gel (3, 4). In the most

recent study (4), "the processed suspensions were stored . . . for a minimum of sixty days to allow system equilibrium to be established."

It was, therefore, of interest to consider in a single study, for a given arbitrary method of preparation, the rheological aging characteristics of Veegum suspensions prepared and stored at different temperatures.

## EXPERIMENTAL

**Sample Preparation.**—All suspensions, 2% by weight, were prepared in a Waring Blendor, model CB-3, in lots of 1 Kg. by the addition of the Veegum to the water. Mixing was 2 minutes at the slowest of the 5 speeds, followed by 5 minutes at the highest speed. The procedure chosen was quite arbitrary and no attempt was made to evaluate effects introduced by deviations from it.

The following temperatures were used for hydration and subsequent storage: Run 1, room temperature, 40, 73, and 88°; Run 2, 6.5°, room temperature, 32, 40, 50, and 60°. The initial water temperature was chosen so that the final hydration temperature did not exceed the values given. Suspensions were made for both Veegum HV and Veegum F. All samples, except for 6.5°, room temperature, and 40° were stored in forced draft air ovens. The 6.5° sample was in a laboratory refrigerator, the room temperature was ambient, and the 40° in a constant temperature room.

**Rheological Examination.**—All evaluations were made at 25° immediately upon attainment of that temperature. The rheometer was the modified Brookfield LVT described elsewhere (5), permitting shear rates up to 20 sec.<sup>-1</sup>. Only in the last stages of the study was the similarly modified RVT available. Because of its higher speeds, shear rates to 45 sec.<sup>-1</sup> were available for samples in the appropriate viscosity range. All rheological measurements were made on aliquots removed as required from bulk storage. No samples were ever reused.

The time intervals for measurement were chosen as convenient for measurement rather than at fixed intervals since the logarithm of time plot was being used to follow changes. Thus samples are compared at corresponding times by graphical interpolation. All interpolations were from plots with point to point joining, rather than from smoothed lines.

Since the sample rheology was time dependent, it

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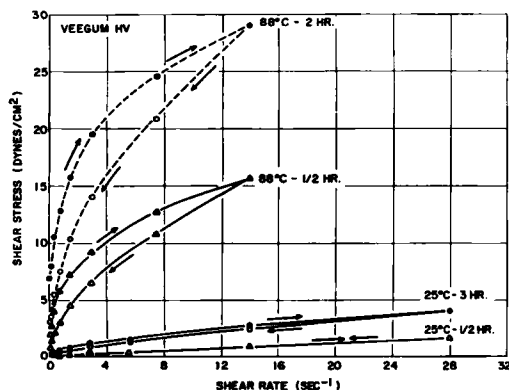


Fig. 1.—Typical rheograms for newly formed Veegum HV mucilages.

was not possible to replicate rheograms in the early hours. At later times, since each rheogram fitted satisfactorily into the pattern of all those preceding it, no attempt was made at replication, except for the example shown in Fig. 2. This is at a period of maximum thixotropy and hence of greatest difficulty in duplication.

With the modified Brookfield in use here, the time constant is such that, in viscous Newtonian systems at very low shear rates, several revolutions of the bob are necessary to reach the steady state reading. Generally, two or three rotations at the low speeds were all that was necessary to attain maximum torque in this study. Immediately upon attaining this value, the speed was increased to the next increment, thus minimizing thixotropic breakdown during the ascending curve. This is the accepted best procedure for systems of this type. All points shown in this study are from the ascending shears only. In Figs. 1 and 2 are shown the gambit of typical rheograms in the initial hours after preparation and after extensive aging, respectively.

**Intrinsic Viscosity Comparison.**—Suspensions of Veegum HV in 0.5*M* sodium chloride were made for 11 concentrations of Veegum in the range 0.01 to 0.4 wt. per cent, using the Waring Blendor as before. These suspensions were made at room temperature, split into two fractions, and were held in tightly sealed bottles at room temperature and 95° for 1 week. A further 2 days were allowed for the 95° sample to cool. The bottles were checked for any weight loss. Viscosity measurements at 25° were run both for ascending and descending speeds using the "O" cup and bob of the Epprecht (Drage) viscometer. The measuring system is ideal for intrinsic viscosity studies on systems where the normal capillary methods are subject to blockage (6). Shear readings were taken over the full range of speeds for both ascending and descending rates of shear. Limiting slopes of shear stress against shear rate extrapolated to zero shear rate were taken as the viscosity of the sample.

## RESULTS AND DISCUSSION

### General Rheology and Aging Characteristics.

As initially prepared, the suspensions were very thin. They showed limited thixotropy and were typically pseudoplastic in both ascending and de-

scending shear curves (see Fig. 1). As aging continued, the yield value character already evident in Fig. 1 became more pronounced; both static and dynamic yield values are evident in Fig. 2. This phenomena and this typical rheogram shape has been discussed elsewhere (7). It should be noted that extensive aging introduced a mild rheopectic behavior into the low shear rheogram replacing the earlier minor thixotropy. More severe shear would have probably shown sufficient thixotropy to mask the very low shear rheopecty. Veegum F exhibited similar properties throughout to Veegum HV but, as is clearly evident from Fig. 2, did not show anywhere near as much build-up of plastic body, by a factor of over 10 in viscosity or shear stress units. This difference is also exhibited in comparing the 10 sec.<sup>-1</sup> curve for HV in Fig. 4 with the 50° isotherm for F in Fig. 5.

In the shear rate permitted by the modified Brookfield LVT rheometer, approximately 0.1 to 20 sec.<sup>-1</sup>, all the 2% Veegum suspensions behaved in this study as almost ideal pseudoplastic systems. Thus a plot of the log of the shear stress,  $T$ , against the log of the shear rate,  $D$  ( $\log T$  vs.  $\log D$ ), gave essentially straight line plots, an example of which is given in Fig. 3. The slope, or Power law index, ranged from 0.70 to 0.33 for the time interval shown in Fig. 1. Characteristics to be noted are the increase in shear stress required with time, and the marked decrease in the slope of the line with increasing sample age. It is more convenient to deal with apparent viscosity,  $\eta_a$ , defined as  $T/D$ , for various given values of the shear rate. The resultant plot, Fig. 4, shows clearly that with age the apparent viscosity becomes increasingly dependent on the shear rate of measurement used.

Recently the application of log viscosity-log time plots for the following of the aging of systems which develop viscous body with time was discussed (8) for use with lotion products. This type of plot was applicable for all the samples studies. Within a set

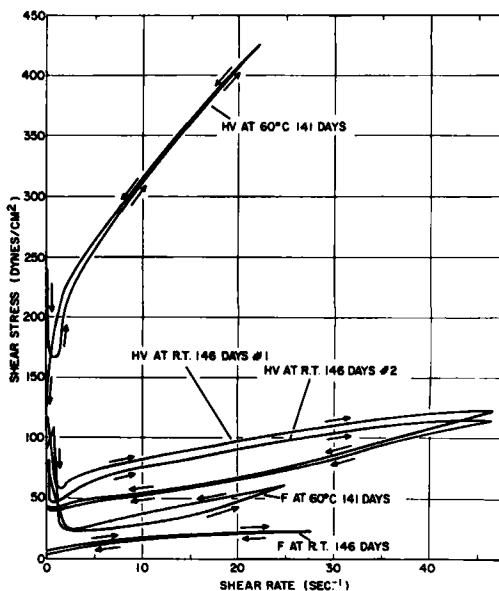


Fig. 2.—Typical rheograms for aged Veegum suspensions.

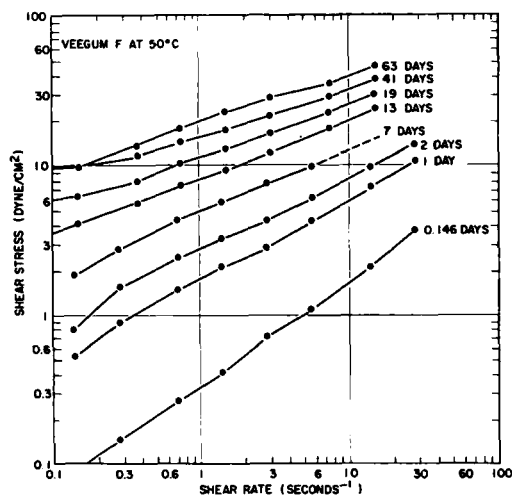


Fig. 3.—Shear stress vs. shear rate curves for a 2% Veegum F suspension prepared and held at 50° for varying periods of time.

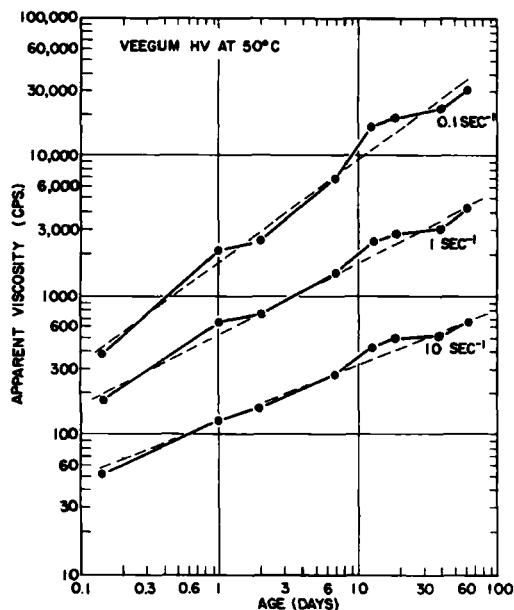


Fig. 4.—Variation of apparent viscosity at different shear rates with time for 2% Veegum HV suspensions prepared at 50°.

of samples prepared at the same time, a series of almost parallel lines for different temperatures of preparation and storage was obtained. An example is shown in Fig. 5. Arbitrarily the apparent viscosity may be compared for any desired shear rate. The general utility of this plot means that

$$\log \eta_D = a \log t + b \quad (\text{Eq. 1})$$

or

$$\eta_D = ct^a \quad (\text{Eq. 2})$$

where  $\eta_D$  is the apparent viscosity at shear rate  $D$  as measured at time  $t$ ,  $a$  is the slope of the line from the plot, and  $b$  or  $c$  are constants which are dependent on the shear of making, temperature, and sample age.

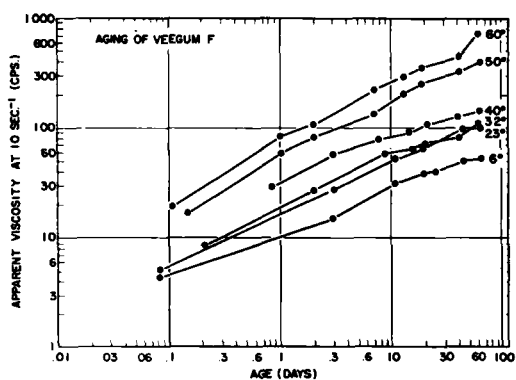


Fig. 5.—Variation of apparent viscosity at 10 sec.<sup>-1</sup> with time for 2% Veegum F suspensions prepared and held at various temperatures.

We have found that this equation is general for age dependent systems (9) and has been applicable over the time range of fractions of an hour to almost 2 years.

In Table I are given values of the constant  $a$  for both Veegums when viscosity is in centipoises and time in days

It is felt that the values of  $a$  are temperature independent over the range examined, and in all probability the values are identical for the two Veegums. Because of the narrow range of  $a$  values it is impossible to tell the nature of the dependency on the logarithm of shear rate, since both plots of  $a$  directly and of  $\log a$  are linear with  $\log D$  over the range of data.

It is of interest to realize that the shear dependency of  $a$  does imply that a static yield value builds with time at a faster rate than does the dynamic viscosity.

Although every effort was made to duplicate making procedures, it was found that, in general, samples made over a year and a half apart tended not to duplicate but rather to yield their own set of parallel lines. This is probably due to minor variations in technique of initial hydration. This, however, did not affect the degree of temperature dependence reported in the next section.

Since the constants  $b$  or  $c$  are so history dependent, they are not reported here. Since the literature (3, 4) so emphasizes the critical dependence of mucilage viscosity upon the making procedure, it is evident that each method of preparation will generate its own set of  $b$  or  $c$  constants.

Samples stored at temperatures at 50° or higher tended to show slight syneresis after prolonged storage although they continued to yield viscosity determinations reasonably in line with the projection from earlier points.

**Temperature Dependence.**—Initially only four temperatures of preparation and storage were used: room temperature, 40, 73, and 88°. Somewhat later, when it was noted that, for any age, the log of the viscosities might obey an inverse temperature law, further samples were prepared. The samples prepared at different times yielded parallel lines for all plots, regardless of the age of the samples. Figure 6 shows for Veegum HV the dependence of the logarithm of the viscosity (at 10 sec.<sup>-1</sup>) on the reciprocal of the absolute temperature for agings of

TABLE I.—DEPENDENCE OF  $\alpha$  OF EQUATION 1 ON SHEAR RATE OF MEASUREMENT AND VEEGUM TYPE USED

Temp. of Measurement, ° C.	Veegum HV			Veegum F		
	0.1 sec. <sup>-1</sup>	1 sec. <sup>-1</sup>	10 sec. <sup>-1</sup>	0.1 sec. <sup>-1</sup>	1 sec. <sup>-1</sup>	10 sec. <sup>-1</sup>
6	0.74	0.58	0.48	0.85	0.60	0.43
23	0.76	0.68	0.43	0.76	0.56	0.45
32	0.58	0.48	0.32	0.77	0.58	0.38
40	0.61	0.38	0.30	0.58	0.48	0.36
50	0.62	0.40	0.32	0.79	0.58	0.45
60	0.83	0.62	0.36	0.70	0.63	0.53
Average	0.69	0.52	0.37	0.74	0.57	0.43

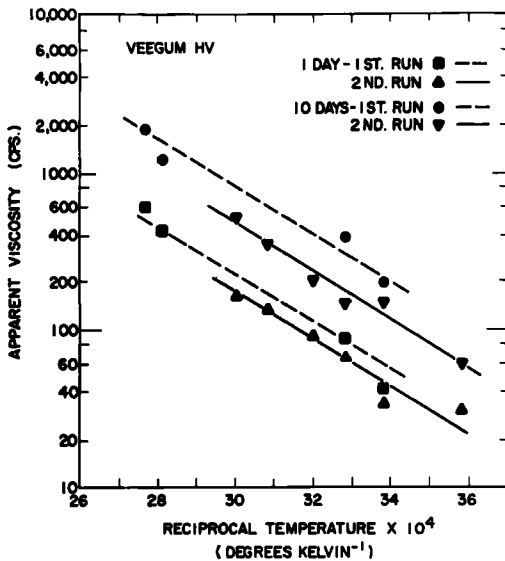


Fig. 6.—Variation of apparent viscosity at 10 sec.<sup>-1</sup> with reciprocal of absolute temperature for 2% Veegum HV suspensions for two different periods of aging.

both 1 and 10 days. The best fits are lines of similar slope through all points of a given set. The same slope was found for Veegum F.

Thus it is apparent that Veegum viscosity build-up follows an Arrhenius activation law relationship

$$2.303 \log \eta = -\frac{E}{RT} + d \quad (\text{Eq. 3})$$

and

$$\eta = fe^{-E/RT} \quad (\text{Eq. 4})$$

where  $\eta$  is in appropriate units,  $T$  is the absolute temperature,  $e$  is the base of natural logarithms,  $d$  and  $f$  are fit constants which are dependent on the units used for  $\eta$  and obviously upon the whole sample history,  $E$  is the apparent activation energy, and  $R$  the gas constant. It is apparent that torque at any shear rate, or similar units of gel measurement can be used for  $\eta$  and would affect only the fit constants  $d$  and  $f$ .

$E$  is then found to have the magnitude of 8000 calories/mole. This would be the activation energy for process of opening up the crystal lattice to water. Since Veegum is slowly hydratable without heat, this is a plausible value for activation.

The normal temperature dependency of viscosity has been the subject of considerable work especially in the polymer field (10). Typical is the simple Andrade equation (11) which has a positive expo-

ponential since all polymer variants normally decrease in viscosity with increasing temperature. In contrast, this system shows a viscous build-up with temperature, the viscosity being a measure of the degree of hydration that has occurred.

**Intrinsic Viscosity.**—All samples in the range of concentration used showed slight thixotropic structure which was lost during the course of the full cycle of measurement. However, within the range of experimental determination, no significant difference between the heated and unheated samples could be detected at the low concentrations. This implies that in the very dilute stage all lattice structures are apparently swollen equally, within the week, or carry equivalent hydration shells, regardless of the temperature of storage during hydration.

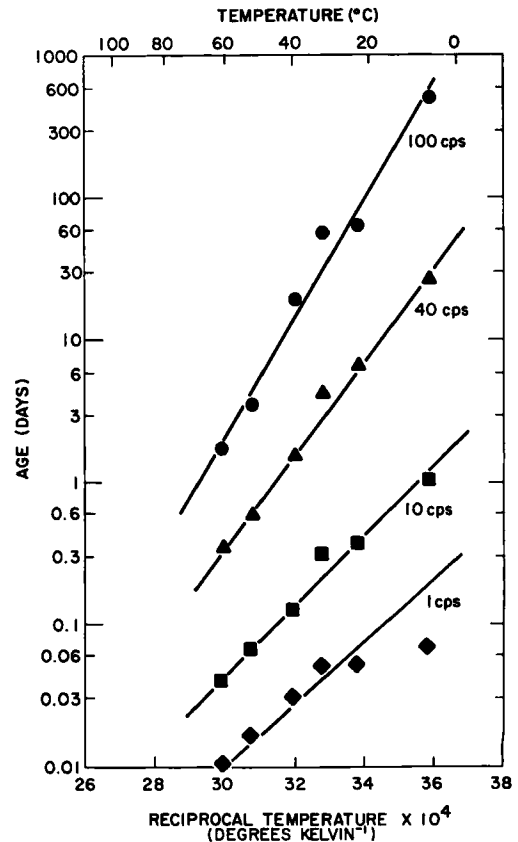


Fig. 7.—Variation of the time required to attain a given viscosity at 10 sec.<sup>-1</sup> as a function of the reciprocal of absolute temperature for 2% Veegum F suspensions.

**General.**—We may combine the equations for the viscosity dependence on aging at constant temperature and on temperature at equal ages into the form

$$2.303 \log \eta_D = 2.303 a \log t - E/RT + g \quad (\text{Eq. 5})$$

$$\text{or} \quad \eta_D = h t^a e^{-E/RT} \quad (\text{Eq. 6})$$

where  $g$  and  $h$  are fit constants which are dependent upon units used and upon preparative history of the sample.

Equation 5 implies that, for any given viscosity level attained during aging, a plot of the reciprocal of temperature and the logarithm of the time required to attain that viscosity will be a straight line. In Fig. 7 are shown such plots for four viscosity levels of Veegum F. The lines are reasonably parallel as is required by the equation. Thus the times required to attain a given level of viscous build-up by varying temperature may be compared.

Equation 5 or 6 or their precursors imply an infinite viscosity with infinite time. This seems to have no practical likelihood of substantiation. Syneresis appears to be the phenomenon which dictates the boundaries within which Eqs. 5 and 6 are valid.

#### SUMMARY

The exponential aging relation has been found to hold for 2% Veegum HV and 2% Veegum F suspensions in water, so that the logarithm of the viscosity is a linear function of the logarithm of

time over a time interval from a few hours to several months.

For samples of equivalent age, an Arrhenius-type relation holds to relate the viscosity with the temperature of preparation and storage. The apparent activation energy for both Veegum HV and Veegum F is about 8000 calories/mole.

The temperature and time relationship may be combined to one general equation which permits time to reach a given viscosity for a given temperature to be determined.

One constant of any of the above relationships is critically dependent on the method of mucilage preparation.

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## Benzoic Acid as an Absorbance Standard in Infrared Spectrophotometry in Pharmaceutical Analyses

By J. P. COMER and A. M. RIBLEY

A solution of benzoic acid in chloroform measured at 5.91  $\mu$  was used to establish absorbance ratios for several drug substances. The ratios were used with daily measurements of benzoic acid as absorbance standards. The precision and accuracy of the technique was found to be equal to the customary method of using the drug substance as a reference standard.

**T**HE PREDICTION of Carol (1) that the use of infrared spectrophotometry in pharmaceutical analyses would increase has certainly been correct. The maintenance of the multitude of chemical standards for infrared spectrophotometry has created many problems. The pharmaceutical laboratories must store and maintain in the original state these standard compounds and also supply governmental agencies with the proper standards. Many analysts (2-6) have reported on various methods for the standardization of instruments. Most of the work concern-

ing the standardization of wavelength and possible use of solid standards does not consider some of the variables encountered in routine control of pharmaceuticals. Variable cell paths, temperature changes, and instrumental responses are corrected normally by performing standard readings of the known compound in solution. The purpose of this investigation was to attempt to find a suitable standard that could be used for quantitative analyses to replace the ever increasing number of individual standards that are encountered in pharmaceutical research programs.

Benzoic acid being readily available in high purity was selected as a trial substance since it has

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