# Flow and Suspension Properties

Basic Concepts of Rheology

Rheology is the study of the deformation and flow of a material when it is subjected to an applied force. When force is applied to a material, the material may respond in a number of ways. One response is for the material to relieve the strain by flowing. In such cases the material is said to be a liquid. A material will always resist an imposed force to some degree. Otherwise, it would have no original form at all. The measure of a flowing liquid to resist an applied shearing force is called its internal friction or viscosity.

Figure 1 illustrates some basic flow concepts.

Figure 1 – Basic flow concepts.
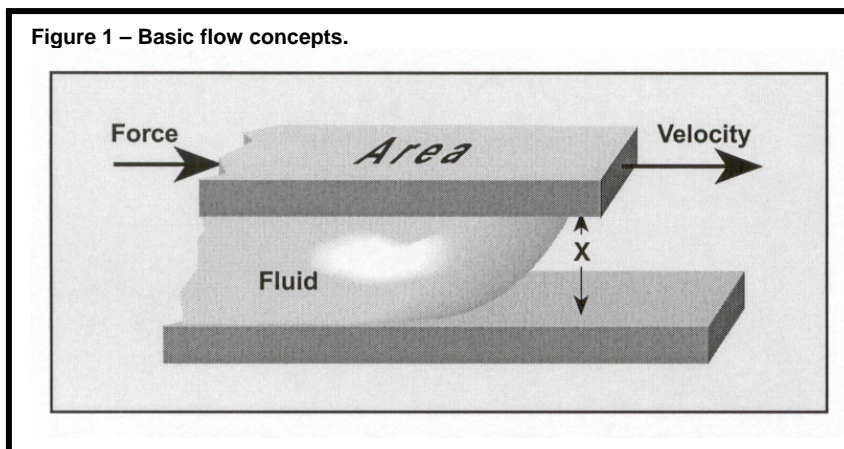
Imagine two parallel plates separated by a distance X. The space between the plates is filled with a fluid. A sufficient, constant force is applied to the top plate (which has a given area) so that this plate moves at a fixed velocity. The force applied to this system may be thought of in terms of shear stress:

Shear Stress = Force/Area

Shear stress is measured in dynes/cm^2. (A dyne is the force needed to accelerate one gram of mass by one cm/sec/sec.)

Liquid next to the top plate flows at the top plate velocity, while liquid next to the stationary bottom plate flows at zero velocity. A velocity gradient exists from top to bottom with intermediate velocities between the plates. This velocity gradient is the response of the system and is called the rate of deformation or shear rate (measured in reciprocal seconds, sec-1):

Shear Rate = Velocity/X

The ratio of shear stress to shear rate is the coefficient of viscosity, more commonly referred to simply as viscosity:

Viscosity = Shear Stress/Shear Rate

The unit of viscosity measurement is the poise (1 dyne-sec/cm^2) or centipoise (100 cP = 1 poise). Viscosity may be thought of as a measurement of the force per unit area required to maintain a certain rate of flow. All flowing materials exhibit viscosity. Some typical values are shown here:

Material	Viscosity, cP
Air	0.01
Water	1
Oils	100 - 100,000

Types of Flow Behavior

There are many types of flow behavior which are broadly categorized as either Newtonian or non-Newtonian. In Newtonian flow, the shear stress and shear rate are always in direct proportion to each other. The viscosity of a Newtonian fluid will always be the same, regardless of the shear stress or shear rate. Newtonian flow behavior is shown in Figure 2: the line will always be straight and will intercept the origin. Examples of Newtonian liquids are water, light oils and other systems in which any dissolved material is low in molecular weight, is non-associating, and has limited interaction with the solvent.

In more complex systems, however, the response to applied stress is nonlinear. These non- Newtonian systems are characterized by large dissolved or solvated molecules, with a tendency to reassociate and a strong interaction with the solvent. In Figure 2, four types of non-Newtonian flow are shown.

Figure 2 – Types of flow.
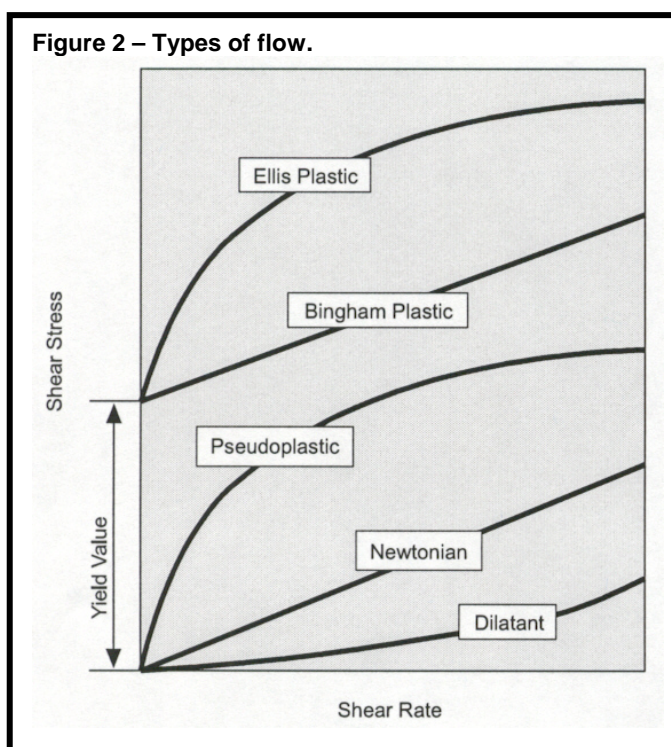
Dilatant — Occurs in suspensions that contain high concentrations of closely-packed solids. Examples: concrete, toothpaste, cake icings.

Pseudoplastic — When viscosity decreases with increasing shear rates, flow characteristics are said to be pseudoplastic. Often referred to as "shear thinning," this flow is encountered with large swollen or dissolved particles, such as emulsions and polymer solutions. Examples: solutions of guar gum, cellulosic thickeners, alginates.

Bingham Plastic — Requires the application of a minimum amount of shear stress before flow begins. Examples: catsup, PVC and styrene polymers.

Ellis Plastic — Similar to pseudoplastic flow except that a minimum amount of shear stress is needed to initiate flow. Example: Carbopol®* polymer gels/creams.

Flow Characteristics of Lubrizol Advanced Materials, Inc. Polymers

Our polymers can be used to provide a wide range of flow properties. High molecular weight, highly crosslinked polymers such as Carbopol® 940 NF, 934 NF, 974P NF, 980 NF and Ultrez 10 NF polymers provide mucilages with a very short flow rheology. Short flow can be characterized as a gelled consistency similar to mayonnaise. In contrast, Carbopol® 941 NF, 981 NF and 971P NF polymers, a lower molecular weight, more lightly crosslinked polymer, provides a fairly long flow rheology. Materials with long flow rheology are "stringy" and flow like honey.

In Figure 3, the shear thinning nature of several Carbopol® polymers is shown. The shear rate is varied by changing the spindle rpm on a Brookfield viscometer. While the viscosity is very high at low rpm, it drops rapidly at higher shear rates. This is a desirable property, for instance, when sag resistance is required (high viscosity at low shear rate), but easy spraying, brushing or troweling is needed (low viscosity at high shear rate).

Thixotropy

Thixotropy is defined as, ". . . a decrease in viscosity under stress, followed by gradual recovery when the stress is removed. The effect is time dependent."[1]

A thixotropic system is one in which (1) shear thinning occurs as stress is increased; and (2) the flow curve is less non-Newtonian when the stress is rapidly removed. A thixotropic material is characterized by the hysteresis loop shown in Figure 4. It occurs, for instance when a dispersed polymer has structure which is broken by the shearing force. Upon standing (no shear stress) the structure reforms with time.

Most Carbopol® polymer gels exhibit little or no thixotropy. Highly viscous media can be spread, stirred or pumped, but when the stress ceases, recovery to the original viscosity is instantaneous.

Figure 3 – Shear-thinning nature of Carbopol polymers

Figure 4 – Thixotropic loop
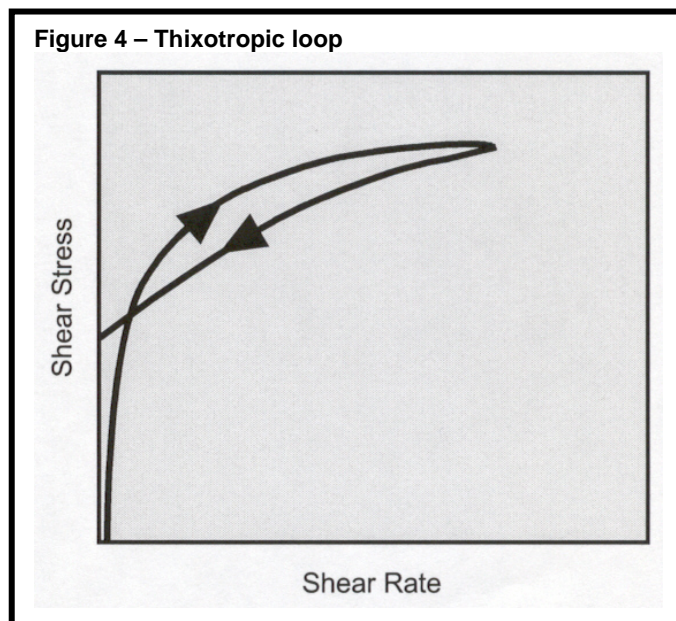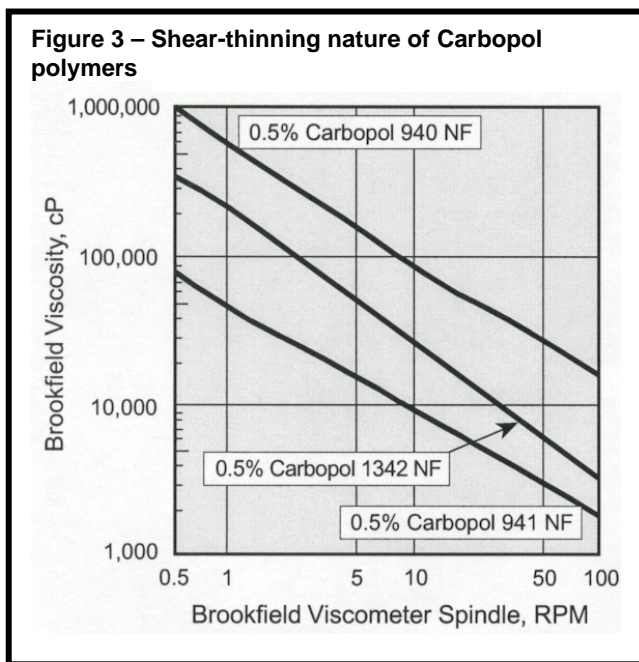
[1]British Standards Institution, Glossary of Rheological Terms, BS 5168: 1975.

Macroviscosity vs. Microviscosity

When a Brookfield viscometer or similar bulk method is used to study a gel, it is the macroviscosity of the material that is determined. While this provides useful information for most purposes, it fails to give an understanding of the nature of the microstructure of the gel.

In the specific case of Carbopol® polymers, Pemulen™* polymeric emulsifiers and Noveon®* AA-1 polycarbophil crosslinked polyacrylic acid based gels, interstitial spaces exist between the swollen gel particles. The liquid in these interstitial spaces has its own viscosity, called microviscosity. The viscosity was measured experimentally by R.Y. Lochhead et al[1] using gold sols with a particle size of 0.1 microns.

In Figure 5, it can be seen that the microviscosity and macroviscosity for a highly crosslinked Carbopol® polymer differ dramatically. In fact, the microviscosity of the interstitial fluid at low Carbopol® polymer concentrations is nearly that of pure water. The amount of interstitial fluid and its microviscosity play an important role in the yield value provided by different Carbopol® polymer grades.

Figure 5 – Macroviscosity vs. Microviscosity
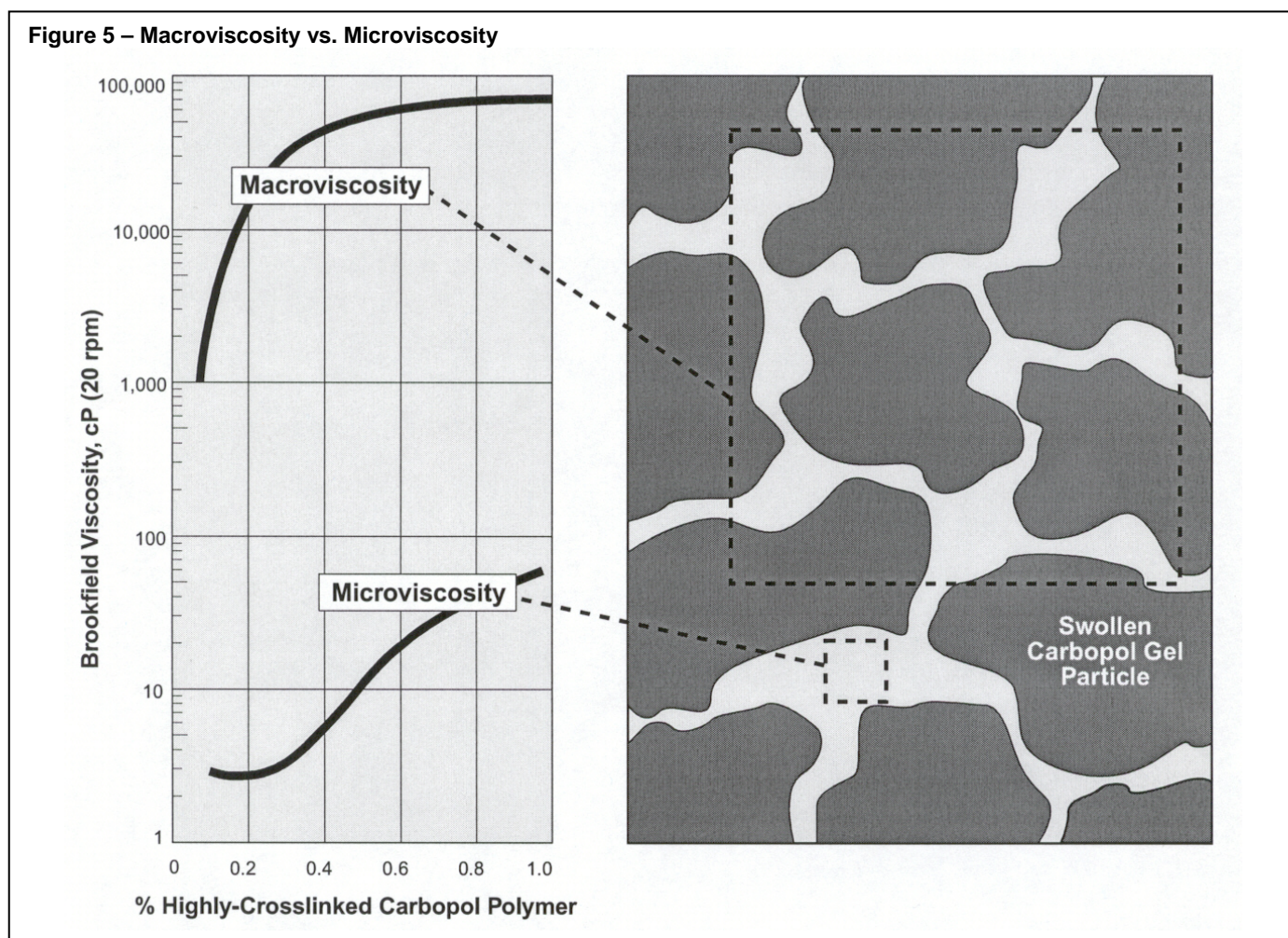
[1]Lochhead, R.Y., Davidson, J.A. and Thomas, G.M., Polymers in Aqueous Media, 1989, pp. 113-147.

Yield Value

Yield value is commonly defined as initial resistance to flow under applied stress. In the case of Bingham and Ellis plastic flow, a minimum shear stress is required to initiate flow. This minimum stress is known as the yield value or yield index. A practical application of yield value is the suspension of particles in a liquid. Unless the force of gravity operating on a suspended particle of a given mass exceeds the liquid's yield value, it will not descend.

If a product has both yield value and shear thinning properties — as Carbopol® polymer based products do — it will appear to be very viscous, but will move easily when force is applied to it.

Yield value is a critical property for a number of applications:

Suspensions — The words "shake well before using" on a label are a sure indication that the product has insufficient yield value. Any particles dispersed in a liquid will be permanently suspended if the liquid's yield value is sufficient to overcome the effect of gravity on those particles.

Vertical Coatings — With sufficient yield value, a gelled coating will not drip or run down a vertical surface.

Emulsions — In the same way that yield value prevents a suspended particle from settling, it can also prevent an oil droplet from rising and coalescing.

Foam — Foam is essentially the suspension of gaseous "particles" in a medium. If that medium is a liquid during processing or in its final form, a minimum yield value is needed for a uniform distribution of the gas.
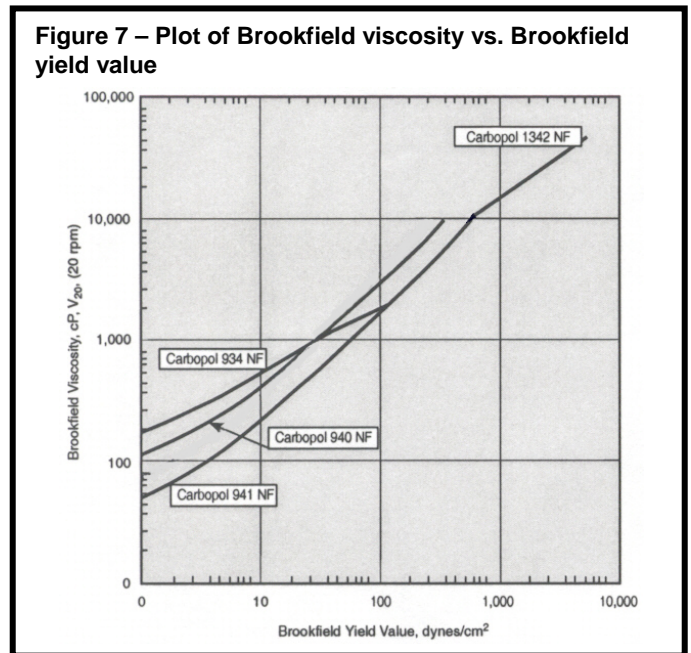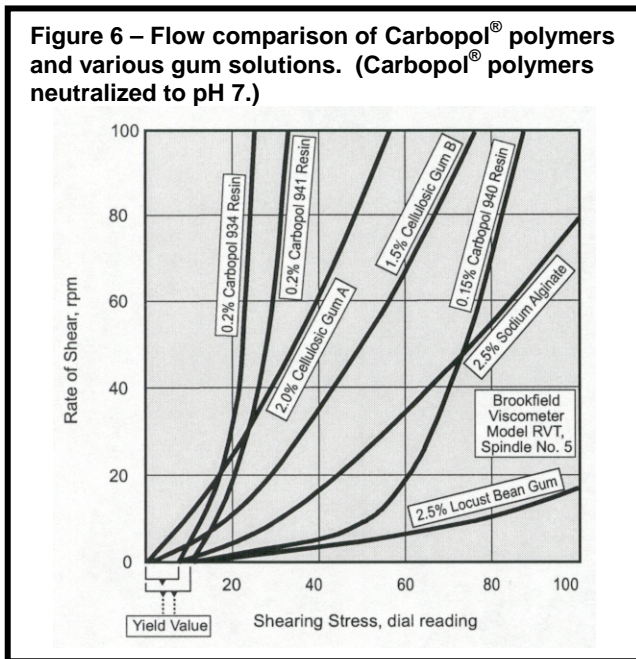
Carbopol® polymers are very effective in forming plastic flow solutions with significant yield value. This can easily be seen in neutralized gels of Carbopol® polymers which are stiff, strong gels at rest, but flow easily when enough force is applied. This enables viscous gels of Carbopol® polymers to be stirred, pumped and spread easily.

Measurement of Yield Value

There are several ways to measure the flow properties of systems which contain Carbopol® polymers including Brookfield viscometer extrapolation, the suspended sphere test method, the B.P. plastometer and the constant stress rheometer (not discussed here).

Brookfield Viscometer Method — The Brookfield RVT viscometer is convenient for measurement at low shear rates. It measures the torque required to rotate a spindle through a sample at 0.05 to 100 rpm. Multiplying the torque dial reading by a constant (depending on the spindle size and speed) gives the apparent viscosity. Increasing the speed results in a corresponding increase in shear rate. In this way, flow properties can be examined by observing torque as spindle speed is varied. Data in Figure 6 represent typical flow curves of water-soluble polymers obtained with a Brookfield viscometer.

Figure 7 shows that Carbopol® 941 NF polymer and its analogues are more efficient in generating high yield values at very low viscosities than the other Carbopol® polymers.

Figure 6 – Flow comparison of Carbopol® polymers and various gum solutions. (Carbopol® polymers neutralized to pH 7.)

Figure 7 – Plot of Brookfield viscosity vs. Brookfield yield value

Because yield value is a zero-shear-rate property, it can be approximated with a Brookfield RVT viscometer and this equation:

Brookfield Yield Value =

$$\frac{\textbf{(Apparent Viscosity at 0.5 rpm — Apparent Viscosity at 1rpm)}}{\textbf{100}}$$

The equation given above shows that a polymer solution can be characterized by yield value as well as viscosity, which is important in permanence of emulsions and suspensions.

The minimum Brookfield Yield Value which is required to permanently suspend a particle can be calculated from the following equation:
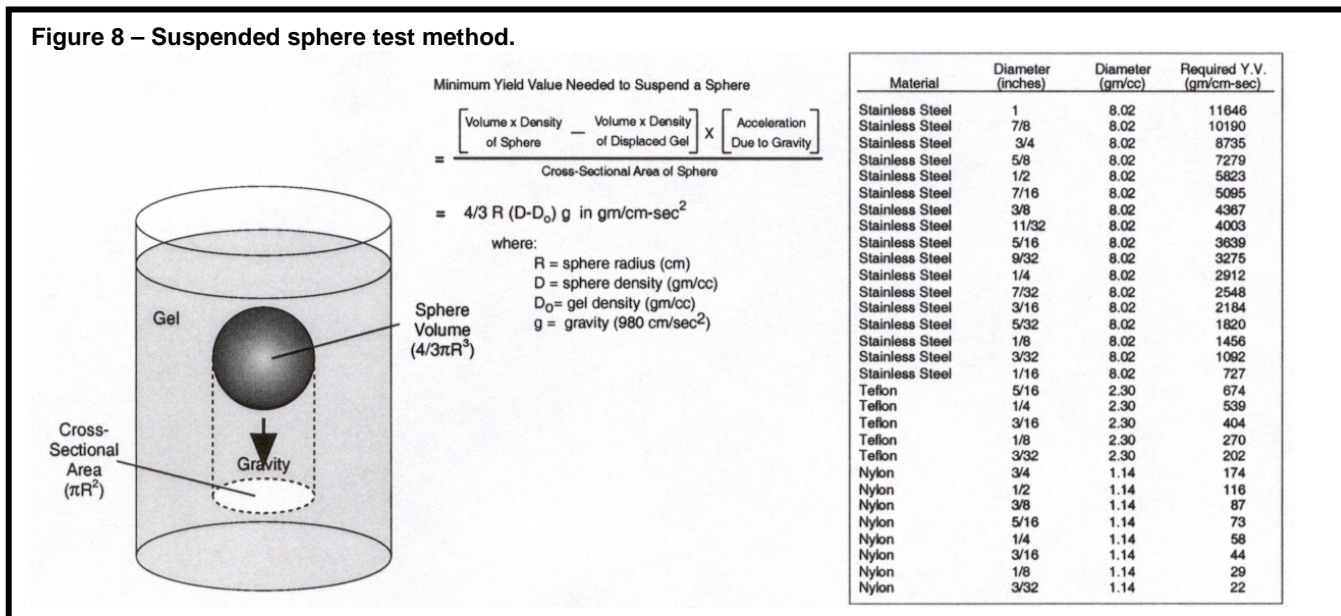
Brookfield Yield Value = [4/3 R (D — D_0)g] in gm/cm-sec^2

where:

R   is the particle radius in cm
D   is the particle density in gm/cc
D_0   is the density of the medium in gm/cc
g   is the acceleration due to gravity in cm/cc

Suspended Sphere Method — The recently-developed suspended sphere method is direct and understandable, albeit time-consuming and impractical for routine evaluations. Up to 30 spheres of varying density and size are suspended in a gel to determine its yield value. As shown in Figure 8, a specific minimum yield value is required to suspend each of these spheres in a water-based gel. The minimum value is dependent on the sphere's density and size.

The location of each sphere in the gel is marked in the container wall and the gel is stored for one month at room temperature. If no appreciable sphere movement is noted, it is considered suspended. The yield value of a particular gel is that associated with the largest, most dense sphere that did not begin settling (from Figure 8). The true gel yield value may be slightly higher (between the suspended sphere and the next larger sphere which began to settle).

Figure 8 – Suspended sphere test method.

| Material	Diameter (inches)	Diameter (gm/cc)	Required Y.V. (gm/cm-sec)
Stainless Steel	1	8.02	11646
Stainless Steel	7/8	8.02	10190
Stainless Steel	3/4	8.02	8735
Stainless Steel	5/8	8.02	7279
Stainless Steel	1/2	8.02	5823
Stainless Steel	7/16	8.02	5095
Stainless Steel	3/8	8.02	4367
Stainless Steel	11/32	8.02	4003
Stainless Steel	5/16	8.02	3639
Stainless Steel	9/32	8.02	3275
Stainless Steel	1/4	8.02	2912
Stainless Steel	7/32	8.02	2548
Stainless Steel	3/16	8.02	2184
Stainless Steel	5/32	8.02	1820
Stainless Steel	1/8	8.02	1456
Stainless Steel	3/32	8.02	1092
Stainless Steel	1/16	8.02	727
Teflon	5/16	2.30	674
Teflon	1/4	2.30	539
Teflon	3/16	2.30	404
Teflon	1/8	2.30	270
Teflon	3/32	2.30	202
Nylon	3/4	1.14	174
Nylon	1/2	1.14	116
Nylon	3/8	1.14	87
Nylon	5/16	1.14	73
Nylon	1/4	1.14	58
Nylon	3/16	1.14	44
Nylon	1/8	1.14	29
Nylon	3/32	1.14	22

This suspended sphere test was performed at ten concentrations, in water, of the suspending aids listed in Table 1. The results of a performance of the suspended sphere test on the listed suspending aids is shown in Figure 9. An attempt was made to select the most effective grade of suspending aid in each group, and to use it in the manner prescribed by the manufacturer. However, certain techniques and product grades may have been overlooked which would have improved the suspending results of one or more suspending aids.

Table 1
SUSPENDING AIDS

Chemical Name	Trade Name	Supplier
Polyacrylic acid	Carbopol® 934 NF Polymer	Lubrizol
Polyacrylic acid	Carbopol® 940 NF Polymer	Lubrizol
Polyacrylic acid	Carbopol® 941 NF Polymer	Lubrizol
Carrageenan	Carrageenan 231	FMC Corp.
Carboxymethyl cellulose	CMC-7H	Aqualon
Xanthan gum	Kelzan S	Kelco
Algin	Kelgin HV	Kelco
Magnesium aluminum silicate	Veegum T	R.T. Vanderbilt
Acrylic emulsion	Acrysol ASE-60	Rohm & Haas
Tragacanth gum	Traganth gum	Rhone-Poulenc
Locust bean gum	Locust bean 175	Rhone-Poulenc
Guar gum	Galactasol 416	Aqualon
Hydroxyethyl cellulose	Natrosol Plus 430	Aqualon
Hydroxypropyl methylcellulose	Methocel J12MS	Dow Chemical
Polyethylene oxide	Polyox WSR-301	Union Carbide
Fumed silica	Cab-O-Sil M-5	Cabot Corp.

Figure 9 – Comparison of yield values
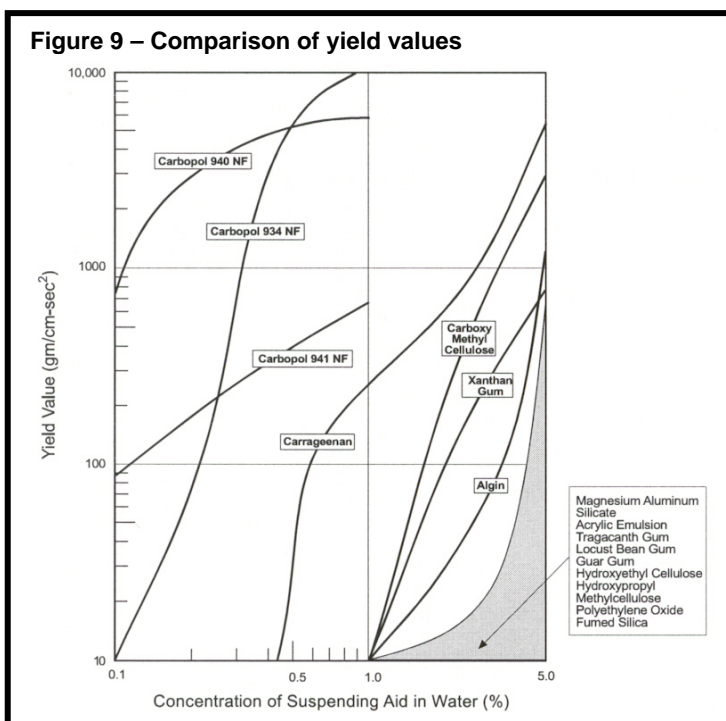
In most of the range examined, a Carbopol® polymer was ten-to-fifty times more efficient in delivering yield value than other suspending aids. If extremely high yield values are required, Carbopol® 934 NF polymer (or its analogues) is a good choice. For most other yield value requirements, Carbopol® 940 NF polymer (or its analogues) is recommended. Although concentrations below 0.1% were not examined here, Carbopol® 941 NF polymer (or its analogues) may be the best choice if very low yield values are needed. (See "Effect of Crosslink Density on Suspending Ability".) The crosslink density of Carbopol® polymers affects their suspending ability at various concentrations.

B.P. Yield Value Determination — The B.P. (British Pharmacopoeia) plastometer value test is based upon the earlier work of Voet and Brand who used a parallel plate rheometer to evaluate the flow properties of printing inks. The method allows for a direct determination of yield value, rather than an approximation.

The apparatus consists of two clear soda-glass plates, 100mm x 100mm x 3mm. The plates are marked with a diamond marker to show center and corner alignment and four sample location points equidistant from the plate center and the four corners. (See Figure 10.) The test is conducted at room temperature.

Four drops of sample gel (applied to each of the four corner points) are sandwiched between the glass plates and the drops are allowed to spread out until equilibrium is reached. The final diameters of the drops are measured and the yield value is calculated as follows:

$$\text{B.P. Yield Value} = \frac{1192}{d^5} \; NM^{-2}$$

where d = average final zone diameter (cm)

B.P. Yield Value Test Procedure

1. Wash plates in a water bath at 24.8 - 25.2°C and dry rapidly before use.

2. Apply 0.1 gram of the gel sample to each of the sample location points on the matted surface of one of the plates.

3. Align the second plate and lower it carefully, matted side downward, onto the lower plate.

4. Add a suitable weight so that the combined weight of the top plate plus applied weight equals 100 grams.

5. Allow the apparatus to stand for 10 minutes and determine the average zone diameter of each of the four sample points using a ruler calibrated in mm.


Figure 10 – B.P. yield value test apparatus.
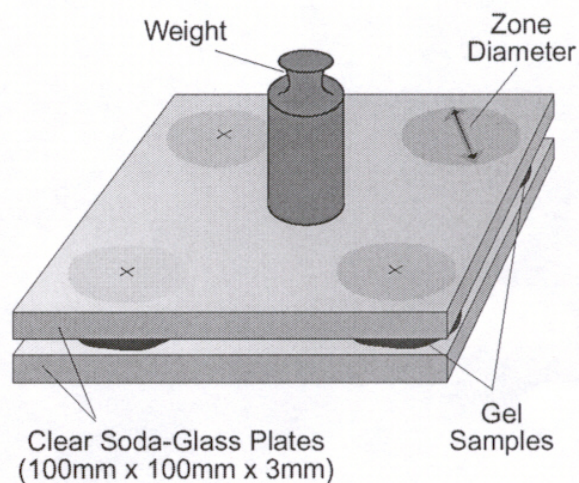
Effect of Crosslink Density on Suspending Ability

Carbopol® 941 NF polymer (and its analogues) is a lightly crosslinked polymer. Because there are few crosslink sites to constrain the polymer, it "opens up" easily at low concentrations. Consequently, the interstitial spaces between the swollen gel particles are eliminated at low concentration and the microviscosity roughly equals the macroviscosity. Due to the limited crosslinking, however, the polymer lacks rigidity. Even at higher concentrations, it provides little additional yield value. (See Figure 11.)

Carbopol® 934 NF polymer and its analogues are heavily crosslinked polymers. Because there many crosslink sites to constrain the polymer, it does not "open up" easily at low concentrations. For this reason, there are large interstitial spaces between the swollen gel particles which have very low microviscosity and cannot suspend insoluble particles well. At high concentrations, however, these rigid gel particles begin to touch producing a system with very high yield value. (See Figure 11.)

**Figure 11 – Effect of crosslink density on suspending**
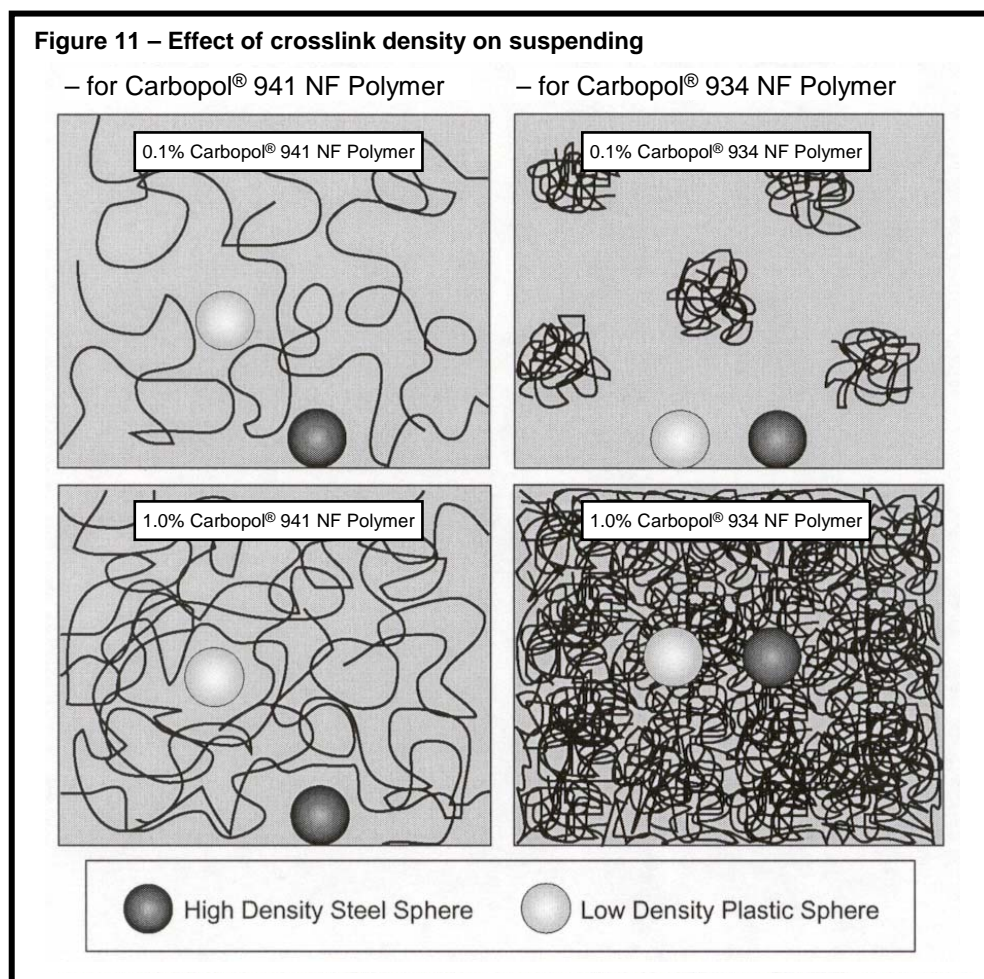
Yield Value vs. Viscosity

The importance of yield value can be seen in Table 2. Several 0.6 mm average diameter silica sand particles were placed in gels based on various thickener types and concentrations. These data dispel the common misconception that high viscosity is needed to create a stable suspension. Viscosity can only slow down the rate of settling, but yield value is needed to create permanent suspensions. The critical minimum required Brookfield yield value range is between 90 and 124.

Table 2

EFFECT OF YIELD VALUE ON SAND SUSPENSION

Material	Brookfield Viscosity, cP	Brookfield Yield Value	Sand Suspension
0.15% Carbopol 941 NF polymer	2,900	500	Permanent
0.15% Carbopol 934 NF polymer	6,350	410	Permanent
3.0% Gum tragacanth (homogenized)	9,740	276	Permanent
3.0% Gum tragacanth (aged two months)	--	144	Permanent
0.18% Carbopol 934 NF polymer	2,420	136	Permanent
0.10% Carbopol 941 NF polymer	1,950	124	Permanent
0.15% Carbopol 934 NF polymer	1,600	90	48 hours
2.5% Locust bean gum	22,800	80	8 hours
1.5% Polyethylene oxide	2,040	40	3 hours
1.5% Sodium carboxymethylcellulose	5,900	36	3 hours
1.5% Guar gum	8,040	32	4 hours
2.5% Sodium alginate	8,360	16	2 hours
3.0% Gum tragacanth (low shear make-up)	940	5	2 hours
2.0% Methyl cellulose	3,200	0	1.5 hours

Another simple demonstration will further illustrate the distinction between viscosity and yield value. In Figure 12, four water-based gels are shown:

A. 2.1% Guar gum
B. 2.3% Carboxymethyl cellulose
C. 6.0% Xanthan gum
D. 0.4% Carbopol® 940 NF polymer

Figure 12 – Viscosity vs. yield value of water-based gels
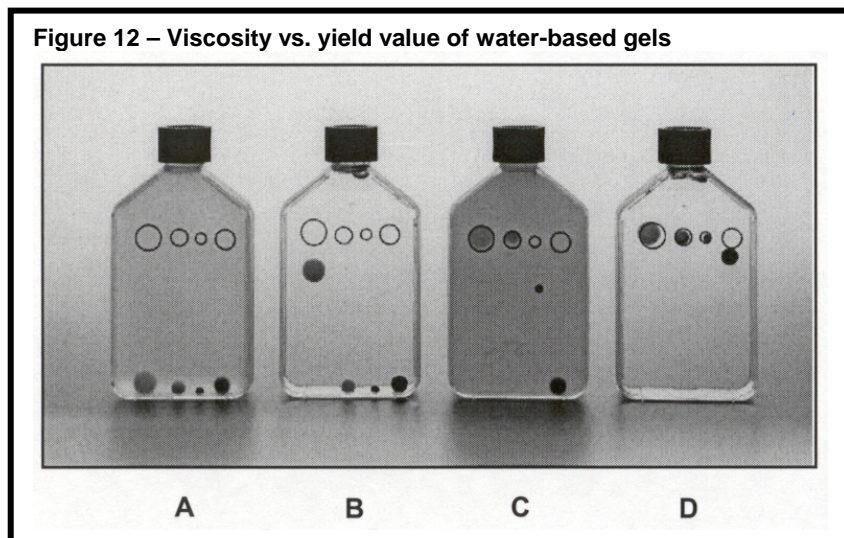
These concentrations were chosen because they all produce the same approximate viscosity: 33,000 cP (Brookfield, 20 rpm, 20°C). Into each of these gels were placed four spheres of varying density and size. The low-density plastic spheres on the left are easier to suspend than the high-density steel spheres on the right. Figure 12 shows how well each gel suspended these spheres after one month of storage. A ring on each marks the initial position of each sphere.

The guar gum and CMC-based gels offered little or no initial resistance to the force of gravity — no appreciable yield value. Even though their viscosity was the same, the xanthan gum and Carbopol® polymer based gels delivered much more yield value or suspending ability. Imagine a pebble dropped into jars of honey and mayonnaise: even though the honey may have high viscosity, it can only slow the rate of settling. It lacks the yield value of the mayonnaise. The yield value provided by Carbopol® polymers gives stability to emulsions and suspensions. In these systems, the problem of stability is one of preventing separation of phases (creaming, breaking of emulsions and settling of solids in suspensions).

Common methods of preventing phase separation include altering droplet or particle size, reducing the difference in density between the dispersed phase and dispersion medium, increasing the viscosity of the dispersion medium, and agitation. Carbopol® polymers give permanently stable emulsions and suspensions by building yield value in the dispersion medium, and controlling the flow rate between the dispersed phase and the dispersion medium. Because yield value is non-directional, the dispersion medium resists movement of particles or oil droplets. The relative shear sensitivity of the various Carbopol® polymers is shown in Figure 13.

Figure 13 – **The effect of varying shear rates on typical Ferranti viscosities of 1% neutralized mucilages of Carbopol® polymers**