6-1957

The Comparison of High and Low Shear Viscometers for Determining Rheological Characteristics in Pigmented Coatings

Philip J. Meyer
Western Michigan University

THE COMPARISON OF HIGH AND LOW SHEAR VISCOMETERS FOR DETERMINING RHEOLOGICAL CHARACTERISTICS IN PIGMENTED COATINGS

Submitted to the faculty of
Western Michigan University
in partial fulfillment of the
prerequisites for the degree
of Bachelor of Science

Philip J. Meyer
Kalamazoo, Michigan
June 5, 1957

INDEX

The Comparison of High and Low Shear Viscometers for Determining Rheological Characteristics in Pigmented Coatings

Introduction

The purpose of this investigation was to determine if there was any relationship between the rheograms of the Hercules High Shear Viscometer and the Stormer Low Shear Viscometer when applied to paper pigmented coatings.

Historical Review

Rheology is the science of the deformation and flow of matter. It is particularly of interest to those in the coating field and other fields dealing with flow in order to find the flow characteristics of material by the use of rheograms. These rheograms are formed by the use of viscometers such as the Hercules High Shear Viscometer and the Stormer Low Shear Viscometer.

Protests raised by industry against the introduction of a scientific form of rheology (1) were; (a) That the science was too complicated for practical use and that no commercial viscometers were available that would give consistency curves for many highly viscous industrial products. (b) The science of rheology aims at a high degree of accuracy and precision. For practical purposes, this is not necessary for the "One-point" methods can be duplicated with precision. (c) Absolute units are not necessary; therefore, nothing is gained by substituting a method that gives absolute values. (d) Even if "One-point" methods are not highly accurate, they are comparable, because they are all made in the same way. The reply to these protests was as follows: (a) The science of rheology is complicated and will continue to become so as more progress is made, as was found with analytical chemistry, spectrophotometry, and many others. (b) The main object in applying a sound rheology to industry is to substitute the multi-point consistency curve for the "One-point" method and therefore has nothing to do with accuracy, because there is no standard method for determining with 100% assurance the actual yield value and plastic viscosity of a material.

(c) The argument about absolute units is also one that causes unnecessary apprehension and confusion. There is no necessity to report measurements in absolute units, except to give the rheologists a common language in which to compare their results. (d) The "One-point" system is a measurement of a single shearing stress and the particular rate of flow of the stress of the material under test on unknown consistency curve. This does not give comparable results because two non-Newtonian consistency curves may pass through the same point, therefore the investigator would report them as being the same material, which would be rheologically incorrect.

Before the work with rheology is taken up, the study of the various types of flow must be understood. The first is the Newtonian or Ideal type of flow. It is characterized (2) as two parallel plates with the space between filled with the test liquid. A tangential shearing stress F is applied to the top plate. The top plate moves the greatest distance, while the bottom one remains constant. All intermediate planes move in linear proportions to the distance from the top plane. Newtonian flow occurs (3) in such liquids as linseed and other vegetable oils in which flow will start under the slightest application of force and the viscosity co-efficient is a constant. This is due to the fact that no structural change takes place, therefore the curve is linear. Since the rate of shear is directly proportional to the tangential force, Newton expressed his idea in the mathematical equation $F = n \frac{dv}{dr}$ where F is shearing stress, v is velocity, r is the distance between plates and n is the co-efficient of viscosity. The next type of flow is the plastic flow (2). In such a system as a clay-water suspension, an initial shearing force has to be applied to overcome the internal frictional resistance to flow. Also the rate of shear is proportional to the stress in excess of the yield value. For a mathematical expression of this, Bingham modified the Newton conception into $F - f = n \frac{dv}{dr}$ where f is the frictional factor. Other examples of this type of flow are materials such as pigmented enamels, paints and inks. The frictional

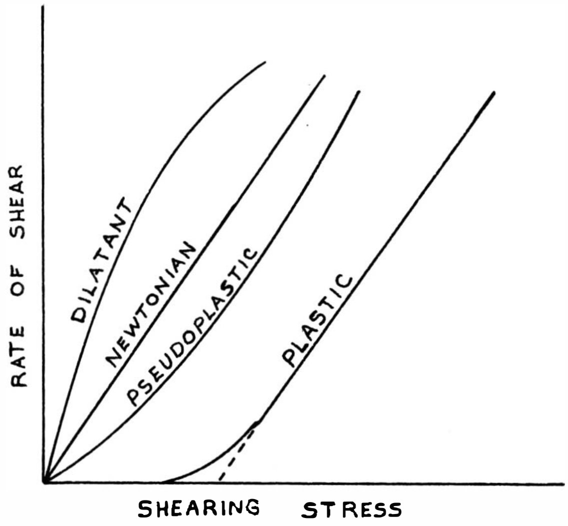
factor which is the force required to produce flow of a plastic is called the yield value. Next is the pseudoplastic type of flow. This type of material poses no real yield value and like Newtonian flow will start under the slightest application of force, but the viscosity co-efficient is not constant. The viscosity co-efficient is not constant because as the material is subject to a shearing stress and permitted to flow, there occurs an alignment of the long molecules, characteristic of this material, parallel to the direction of flow, without structural linkage at high rates of shear. This produces a curve convex to the stress axis, with the up and down curves coinciding, regardless of time. Materials of this type are resins, tars, and heavy oils. The fourth type of flow is dilatant. It is characterized by a non-linear flow curve where large increases in the shearing stress are required to produce small increases in the rate of shear. This is caused by particle deflocculation and concentration, the interparticle space being just sufficient in volume to absorb all the vehicle present. All four of these types of flow give specific types of curves described with each, but there is another type of flow curve called thixotropy. Thixotropy is usually defined (4) as a reversible gel-solution transformation. If a material of this type is allowed to rest undisturbed for a period of time, an internal structure is formed within the material. When shearing begins, enough of these bonds are broken to permit motion, and if shearing action continues at the same rate, more and more bonds are broken, until their rate of destruction equals their rate of formation. If shearing is increased, a new equilibrium is formed. The up curve of the rheogram is non-linear; an increase in shearing stress produces a disproportionately greater increase in rate of shear. The action is non-chemical and isothermic. There are two parts to this curve, the up and down curves which do not coincide, forming a hysteresis loop.

Before going on, a few terms should be defined:

Viscosity - the resistance of a rheological material, such as liquids and plastics, to flow

Coefficient of Viscosity -	the dynes of shearing stress necessary to induce a unit rate of shear. Its unit is the poise.
Rate of Shear -	the rate of shear between two parallel planes is their relative viscosity with respect to each other, divided by the distance between them. Its dimensions are velocity divided by distance. It is recorded as reciprocal seconds.
Shearing Stress -	the force applied by a viscometer to produce flow per unit area.

Below is a graph which shows the various types of flow curves:



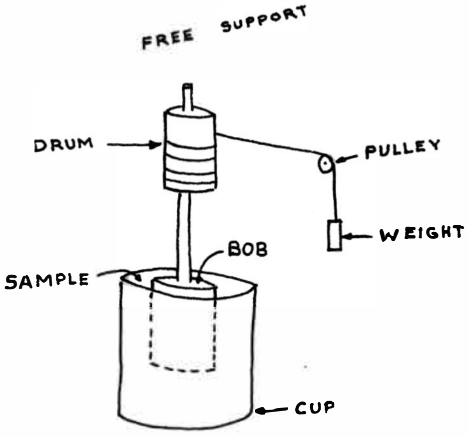
There are various types of viscometers, some of which are listed below, showing their desirable and undesirable features:

FEATURES OF VISCOMETERS

Type of Viscometer	Undesirable Features	Desirable Features
Cup	The orifice is too short to produce streamlined flow. There is no method of changing the shearing stress so that up and down consistency curves can be produced.	Quick and easy to manipulate. Easy to clean. Usually available on the market.
Falling Ball	Not easily adapted for producing consistency curves. Many balls of different weights would have to be employed to produce satisfactory curves. This would be awkward and time consuming.	Temperature control possible. Well suited for liquids where a single point method is satisfactory. In such cases, these instrument can be made to give very accurate results.

Type of Viscometer	Undesirable Features	Desirable Features
Rising Bubble	Not easily adapted for making consistency curves. Bubbles of different sizes might be used for obtaining different rates of shear, but this would be of no value if the yield value altered the shape of the bubble or prevented it from rising.	Inexpensive and easy to operate. Suitable for approximate measurements of the viscosities of liquids of Newtonian type.
Capillary Tube	The flow of plastic materials of the pigment - vehicle type can't give linear curves in these viscometers; consequently, plastic viscosity and yield values can't be calculated. These instruments are also unsuitable for obtaining hysteresis for thixotropic materials.	Excellent for Newtonian liquids. Easy to control the temperature.
Oscillating Discs	These instruments are not actually undesirable. They are constructed so that they do not differ substantially from rotating viscometers. If a selection must be made between the two, it is better to select the rotational viscometer as it is easier to apply the plastic material.	Temperature control is easy. Can be used for producing consistency curves.
Rotating Viscometers	For temperature control, the rotating cup type requires the installation of a water type shaft in a temperature control bath. The rotating bob type requires the change in weight for every point on the consistency curve. This is troublesome and time consuming.	Easily adapted for the consistency curve method.

One type of viscometer which is used by industry is the Stormer Low Shear Viscometer. (3) With this viscometer, the sample is put into the cup which is fixed and the bob is made to rotate by placing weights on the pan. The speed for a given weight is a measure of the consistency. The time for which the bob takes to make one hundred revolutions is used to calculate the revolutions per minute which are plotted against the torque. The following is a diagram of Stormer Viscometer:



MODIFIED STORMER

A second type of viscometer which is used by industry is the Hercules High Shear Viscometer. (4) The Hercules High Shear Viscometer is designed to study the flow properties of high-solids pigment suspensions. It provides analytical rheological data at rates of shear above the levels where radical changes in the fluid behavior of the suspensions becomes apparent and is therefore a tool useful in the intelligent interpretation of rheological data obtained from complex systems, which are to be applied industrially at high rates of shear. With low shear viscometers, it might be difficult, if not impossible, to obtain any information which would be of value in predicting the performance of these suspensions when subjected to high shear. The reason for this lies in the nature and magnitude of the structural viscosity effects found in most high-solids pigment suspensions which were discussed at the start of this paper.

The Hercules High Shear Viscometer is designed so that rates of shear above 5,000 reciprocal seconds are easily employed which may be compared with a maximum of 7 at 45 revolutions per second and 21 at 100 revolutions per second for the Stormer.

High rates of shear are made possible by rotating the bob instead of the cup, and recording the torque developed by the receiver, which holds the cup. The central part is a drill press. When the bob is rotated, torque is transmitted

through the liquid which tends to rotate the cup and receiver. The torque developed by the receiver is an inverse function of the clearance between the face of the bob and the wall of the cup and is directly proportional to the speed with which the bob is rotated and the apparent viscosity of the material being tested. The torque is measured in terms of the linear deflection of a calibrated set of springs.

The chuck and bob are rotated by power transmitted from a Graham variable speed drive. This drive permits continually variable bob speeds from 0 to 1050 revolutions per minute. The speed setting of the Graham transmission is changed by a remote control speed dial and flexible cable arrangement. This assembly permits easy adaption of a simple yet useful automatic recording apparatus.

Experimental Procedure

The purpose of this investigation was to see if there is any relationship between the Hercules High Shear Viscometer and Stormer Low Shear Viscometer.

To accomplish this comparison, rheograms from the two viscometers were made of clay, titanium dioxide, satin white, calcium carbonate, Dow Latex 512K, alpha protein, Argentine casein, 25% Dow Latex 512K and 75% alpha protein, 50% Dow Latex 512K and 50% alpha protein, 75% Dow Latex 512K and 25% alpha protein, and combination of clay with Dow Latex 512K and alpha protein.

Preparation of Clay Slurries

Edgar Brothers predispersed clay was used, with 650 grams dispersed in 350 ml of water. After rheograms were made from this dispersion, the solids were reduced to 60% with water for further viscosity determinations.

Preparation of Titanium Dioxide Slurries

Titanox W. D. was used, with 500 grams dispersed in 500 ml of water. After rheograms were made from this dispersion, the solids were reduced to 45% with water for further viscosity determinations.

Preparation of Calcium Carbonate Slurries

Calcium carbonate slurries were prepared by adding slowly 500 ml of water to 500 grams of the calcium carbonate. After rheograms were made from this dispersion, the solids were reduced to 46% with water for further viscosity determinations.

Preparation of Sating White Slurries

Satin White slurries were prepared by adding to 500 grams of wet slaked lime (equivalent to 160 grams dry), 423 ml of water, and adding to this as rapidly as possible 220 grams of aluminum sulfate and 25 grams of anhydrous sodium sulfate dissolved in 250 ml of water. It was mixed for 30 minutes after the alum was added. It was then diluted to 19% solids, rheograms made,

and then diluted with water to 15% solids for further viscosity determinations.

Preparation of Alpha Protein Solution

Alpha protein was prepared by taking 100 parts alpha protein, 450 parts water, agitating moderately, and allowing to soak for 15 minutes. Ten per cent ammonium hydroxide was added (dissolved to make 500 parts) under agitation and heated to 135 F for one hour. It was then cooled to room temperature before using.

Preparation of Casein Solution

Casein was prepared by taking 100 parts casein, 608 parts water, agitating and soaking for 15 to 30 minutes. To this was added 3.25 parts sodium hydroxide under agitation and heated to 140 F until dissolved. It was then cooled to room temperature before using.

Preparation of Combinations of Dow Latex 512K and Alpha Protein

A combination of 25% Dow Latex 512K and 75% alpha protein was prepared by mixing 38 grams (400 ml) of alpha protein and adding 12.7 grams (26 ml) of Dow Latex 512K under agitation.

A combination of 50% Dow Latex 512K and 50% alpha protein was prepared by mixing 38 grams (400 ml) of alpha protein and 38 grams (79 ml) of Dow Latex 512K under agitation.

A combination of 75% Dow Latex 512K and 25% alpha protein was prepared by mixing 38 grams (400 ml) of alpha protein and 114 grams (238 ml) of Dow Latex 512K.

Preparation of Combinations of Clay, Dow Latex 512K and Alpha Protein

A clay dispersion was prepared by adding slowly 300 ml of water to 700 grams predispersed clay.

A coating color was then prepared of 70 grams dry clay (100 ml of above dispersion) and 11.2 grams (23.3 ml) of Dow Latex 512K. The clay was added slowly to the Dow Latex 512 K under agitation.

A second coating color was then prepared by adding 140 grams of dry clay (200 ml of above dispersion) to a combination of 11.2 grams (118 ml) of alpha protein and 11.2 grams (23.3 ml) of Dow Latex 512 Kunder agitation.

A third coating color was prepared by adding 140 grams of dry clay (200 ml of above suspension) to 22.4 grams (236 ml) of alpha protein under agitation.

Discussion of Results

Rheograms of the 65% solids clay slurries showed dilatant flows on the Hercules High Shear Viscometer and thixotropic - dilatant flows on the Stormer Low Shear Viscometer. The 60% solids clay slurries produced dilatant curves on both viscometers. This is shown in Chart No. 1.

The 50% solids titanium dioxide slurries show essentially plastic flows on the Hercules High Shear Viscometer and anomalous flows with thixotropic, plastic, and dilatant characteristics on the Stormer Low Shear Viscometer. The 45% solids titanium dioxide slurry produced a plastic curve on the Hercules High Shear and a dilatant curve with yield value on the Stormer Low Shear. Chart No. 2 shows these curves.

The rheograms of the 50% solids calcium carbonate slurries showed thixotropic - plastic flow on both the Hercules and Stormer viscometers with the latter showing the wider thixotropic loop and a more distinct yield value. The 46% calcium carbonate slurries produced thixotropic - plastic flow on the Hercules High Shear Viscometer and dilatant flow with a yield value on the Stormer Low Shear Viscometer. This is shown in Chart No. 3.

The 19% solids satin white slurries produced plastic curves on the Hercules High Shear Viscometer and on the Stormer Low Shear Viscometer. However, the yield value on the Stormer was more distinct. The 15% solids produced a plastic rheogram on the Hercules High Shear Viscometer and a dilatant rheogram with yield value on the Stormer Low Shear Viscometer. Again the yield value was more distinct with the Stormer Low Shear Viscometer. Chart No. 4 shows this.

The Hercules High Shear Viscometer showed Newtonian flow while dilatant flow was shown with the Stormer Low Shear Viscometer using 48% Dow Latex 512K. These curves may be seen in Chart No. 5.

The rheograms of the Hercules High Shear Viscometer showed Newtonian flow while the Stormer Low Shear Viscometer showed anomalous flow with 9.5% alpha protein solutions. Chart No. 5 shows these rheograms.

The 14% casein showed pseudoplastic flow on the Hercules High Shear Viscometer while the Stormer Low Shear Viscometer showed dilatant flow. This is shown in Chart No. 6.

The 25% Dow Latex 512K and 75% alpha protein produced a Newtonian flow curve on the Hercules High Shear Viscometer while the Stormer Low Shear Viscometer showed anomalous flow. This may be seen in Chart No. 6.

The Hercules High Shear Viscometer showed a Newtonian curve while the Stormer Low Shear Viscometer showed anomalous flow with the 50% Dow Latex 512K and 50% alpha protein. Chart No. 7 shows this.

The 75% Dow Latex 512K and 25% alpha protein flow diagrams showed Newtonian flow with the Hercules High Shear Viscometer and anomalous flow with the Stormer Low Shear Viscometer. Chart No. 7 shows these flow diagrams.

The rheograms of the Hercules High Shear Viscometer showed Newtonian flow while the Stormer Low Shear Viscometer showed dilatant flow with the coating color, 70 grams dry clay and 11.2 grams Dow Latex 512K. This is shown in Chart No. 8.

The Hercules High Shear Viscometer showed Newtonian flow with the coating color, 140 grams dry clay, 11.2 grams Dow Latex 512K and 11.2 grams alpha protein while the Stormer Low Shear Viscometer showed dilatant flow. This may be seen in Chart No. 8.

The coating color, 140 grams dry clay and 22.4 grams alpha protein showed Newtonian flow with the Hercules High Shear and dilatant with the Stormer Low Shear. Chart No. 9 shows this.

Experimental Results

Material Used	Type of Flow: Hercules	Type of Flow: Stormer
Clay		
High solids	Dilatant	Thixotropic - Dilatant
Low solids	Dilatant	Dilatant
Titanium Dioxide		
High solids	Plastic	Anomalous
Low solids	Plastic	Dilatant
Calcium Carbonate		
High solids	Thixotropic - Dilatant	Thixotropic - Dilatant
Low solids	Thixotropic - Dilatant	Dilatant
Satin White		
High solids	Plastic	Plastic
Low solids	Plastic	Dilatant
Dow Latex 512K	Newtonian	Dilatant
Alpha Protein	Newtonian	Anomalous
Casein	Pseudoplastic	Dilatant
25% Dow Latex 512K 75% Alpha Protein	Newtonian	Anomalous
50% Dow Latex 512K 50% Alpha Protein	Newtonian	Anomalous
75% Dow Latex 512K 25% Alpha Protein	Newtonian	Anomalous
Clay - Dow Latex 512K	Newtonian	Dilatant
Clay - Dow Latex 512K and Alpha Protein	Newtonian	Dilatant
Clay - Alpha Protein	Newtonian	Dilatant

Summary of Results

From the results of the rheograms, it was noted that:

1. Yield values are more distinct in the rheograms from the Stormer Low Shear Viscometer than from the Hercules High Shear Viscometer.
2. Some Newtonian flows on the rheograms of the Hercules High Shear showed up slightly dilatant on the Stormer Low Shear.
3. The Stormer Low Shear Viscometer showed wider thixotropic loops than did the Hercules High Shear Viscometer.
4. Plastic, pseudoplastic, and dilatant flows are distinct on both viscometers, but the Stormer Low Shear Viscometer curves are more accented.

Conclusion

From the experiments reported, it may be concluded that the Stormer Low Shear Viscometer gives a more sensitive rheogram than does the Hercules High Shear Viscometer. This might be due to the fact that the Hercules High Shear Viscometer developes a change in shearing rate and force more rapidly than does the Stormer Low Shear Viscometer.

Chart No. 1 Rheograms of Clay

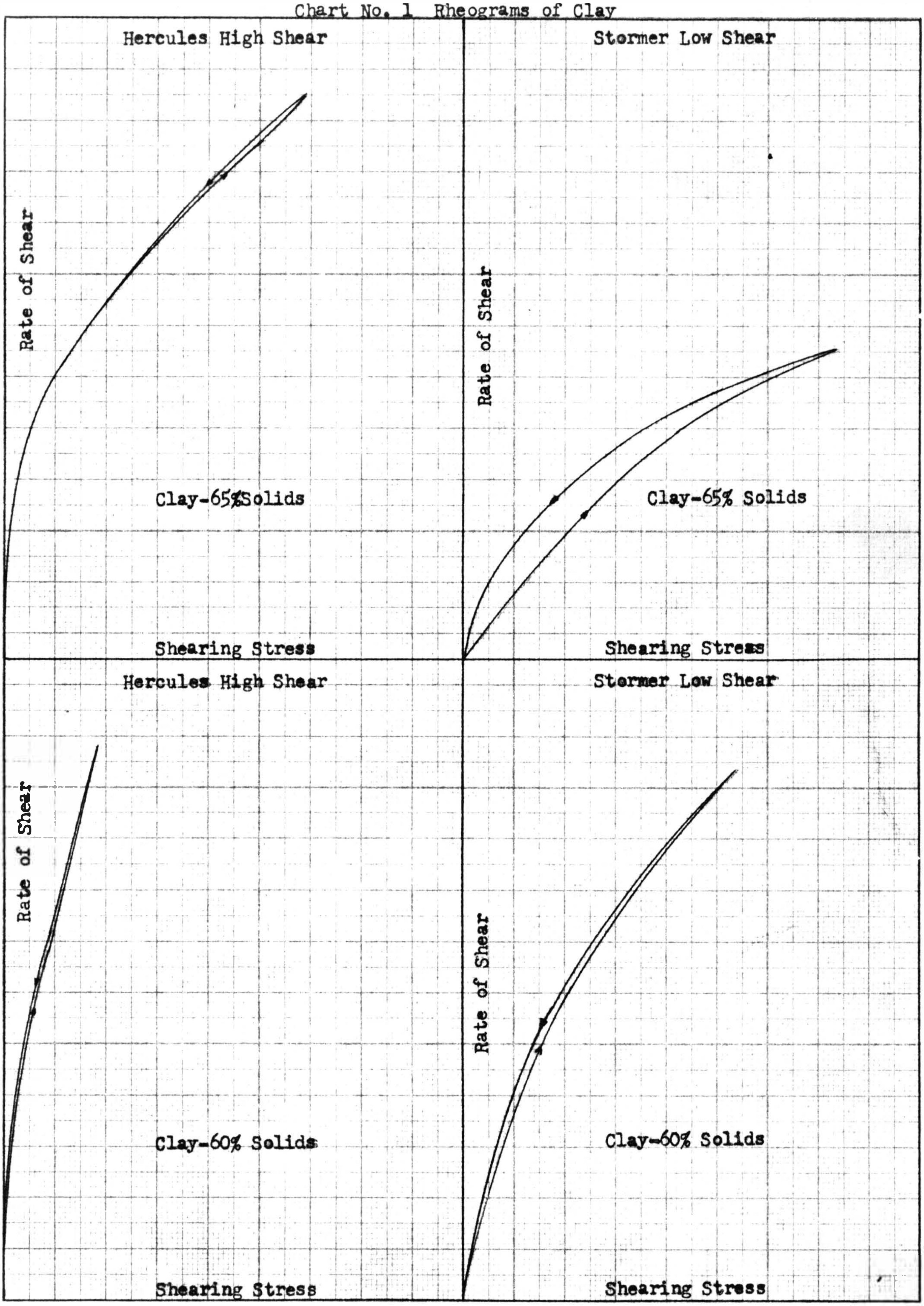


Chart No. 2 Rheograms of Titanium Dioxide

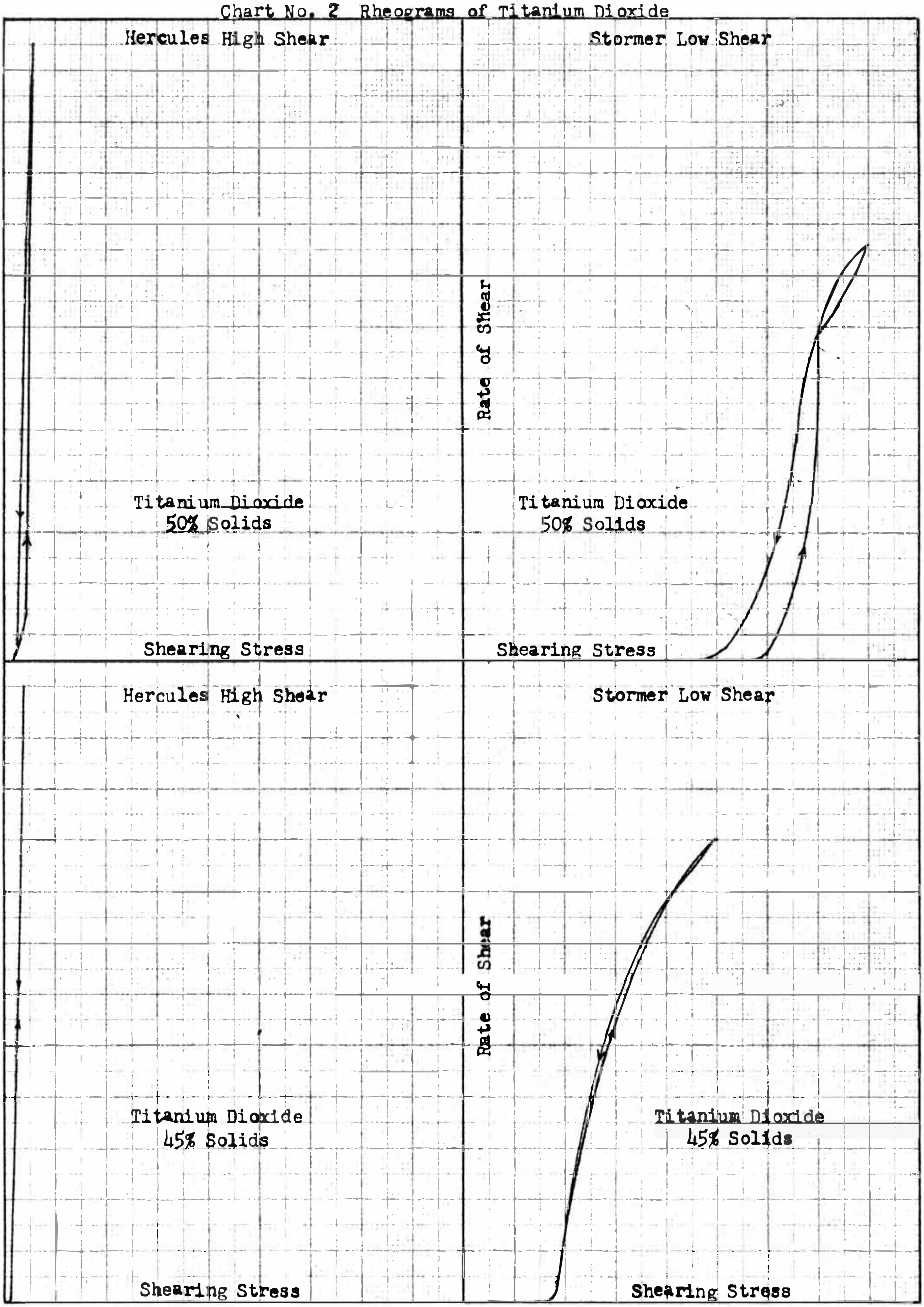


Chart No. 3 Rheograms of Calcium Carbonate

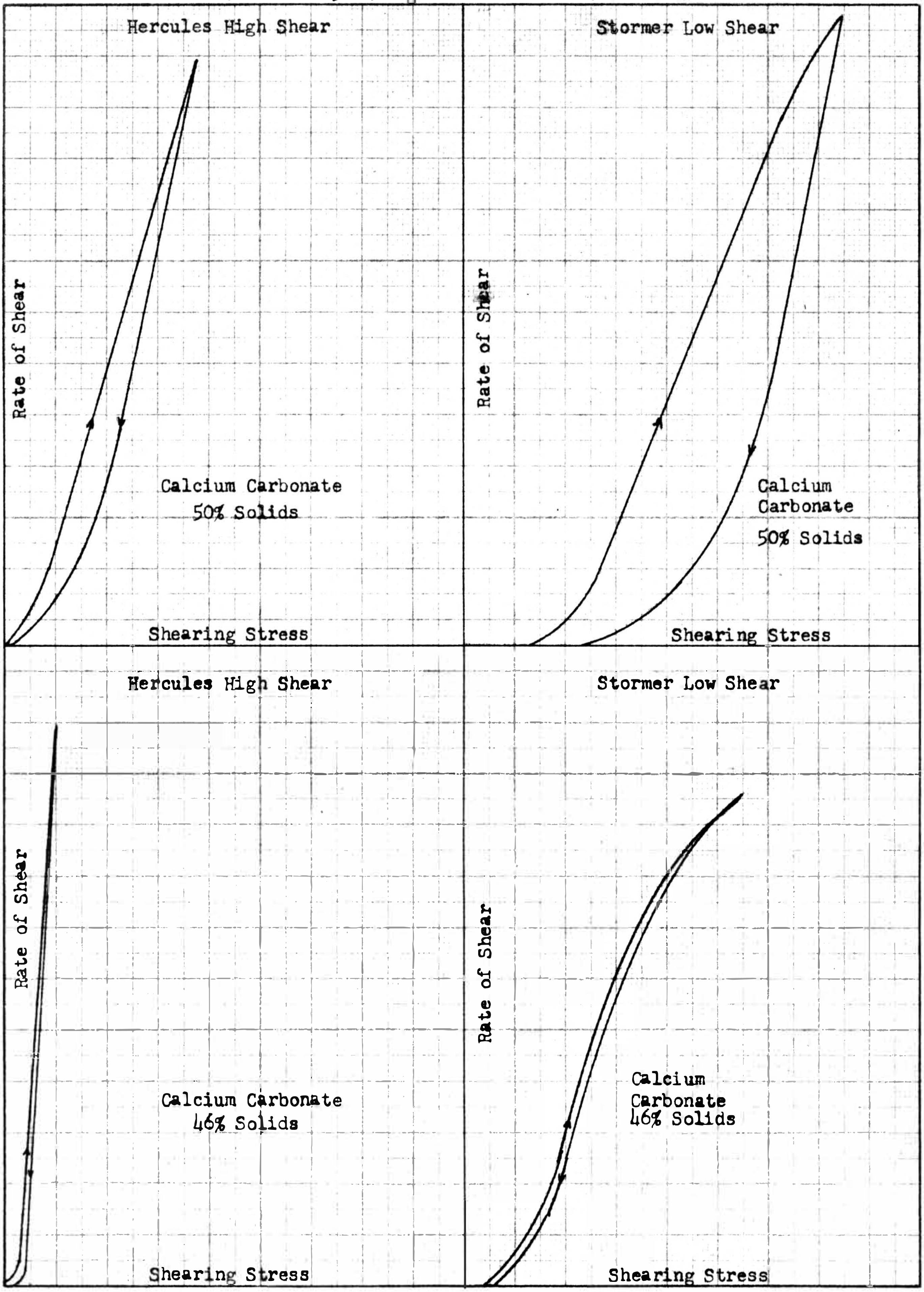


Chart No. 4 Rheograms of Satin White

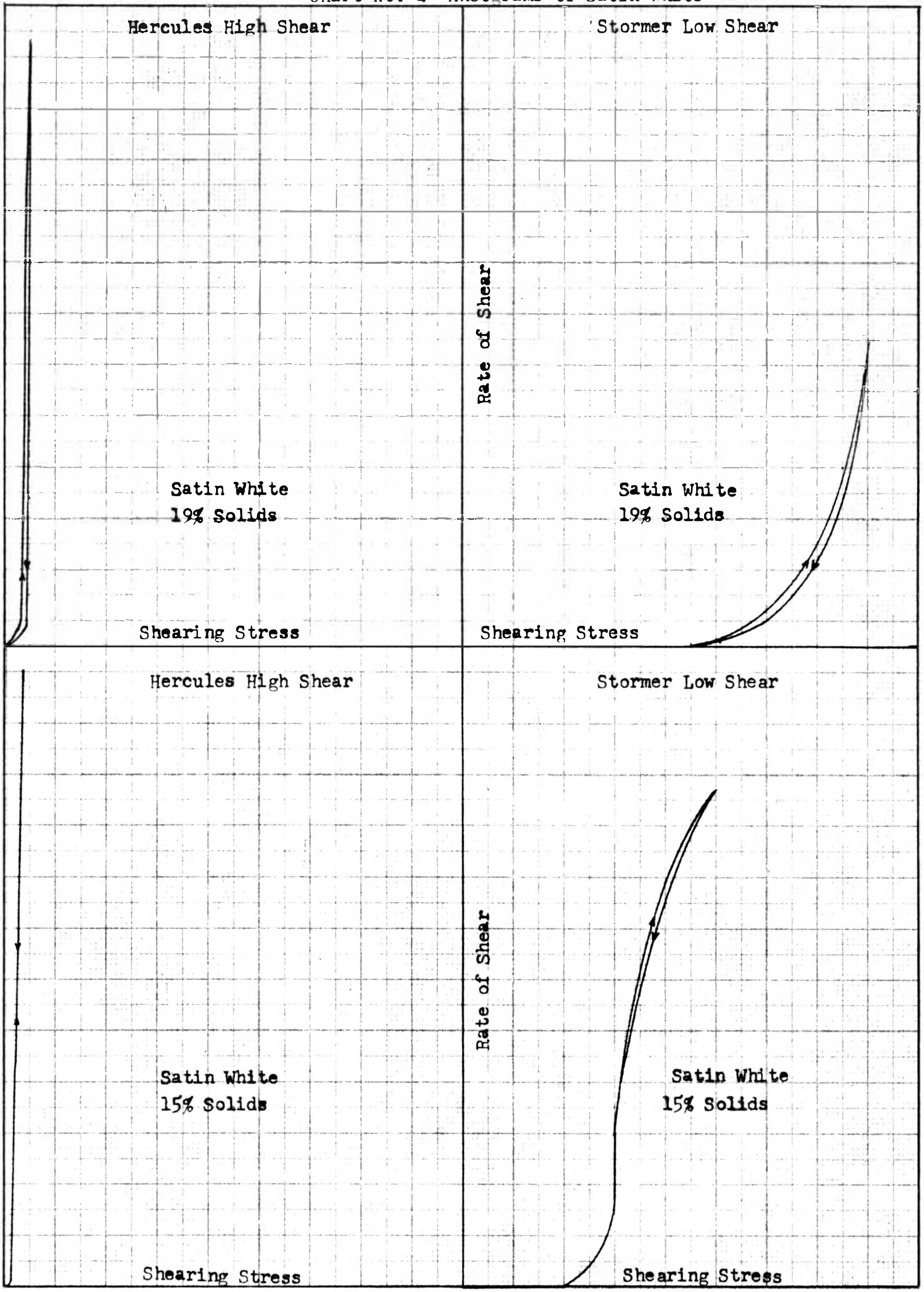


Chart No. 5 Rheograms of Dow Latex 512K and Alpha Protein

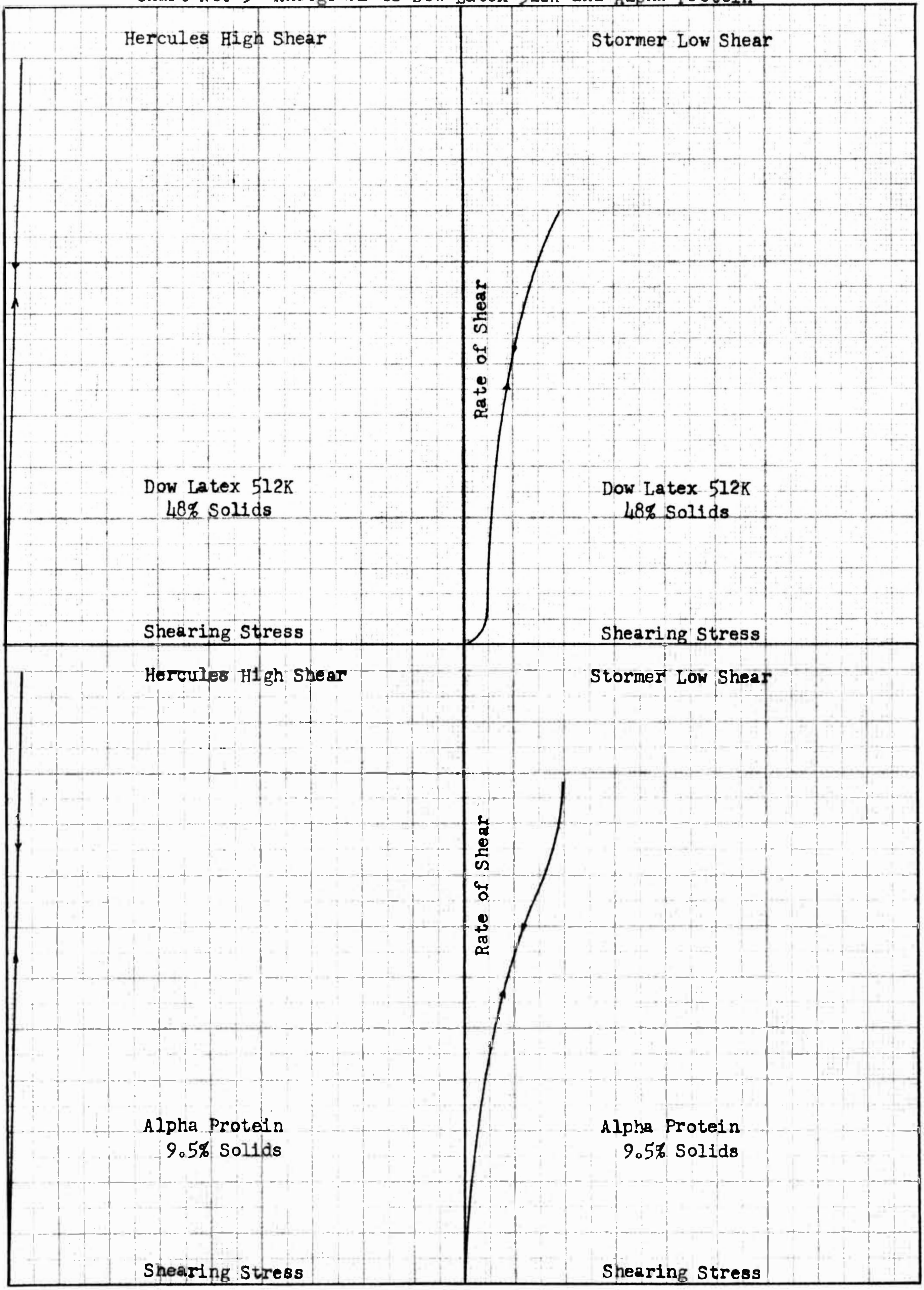


Chart No. 6 Rheograms of Casein-Dow Latex 512K and Alpha Protein

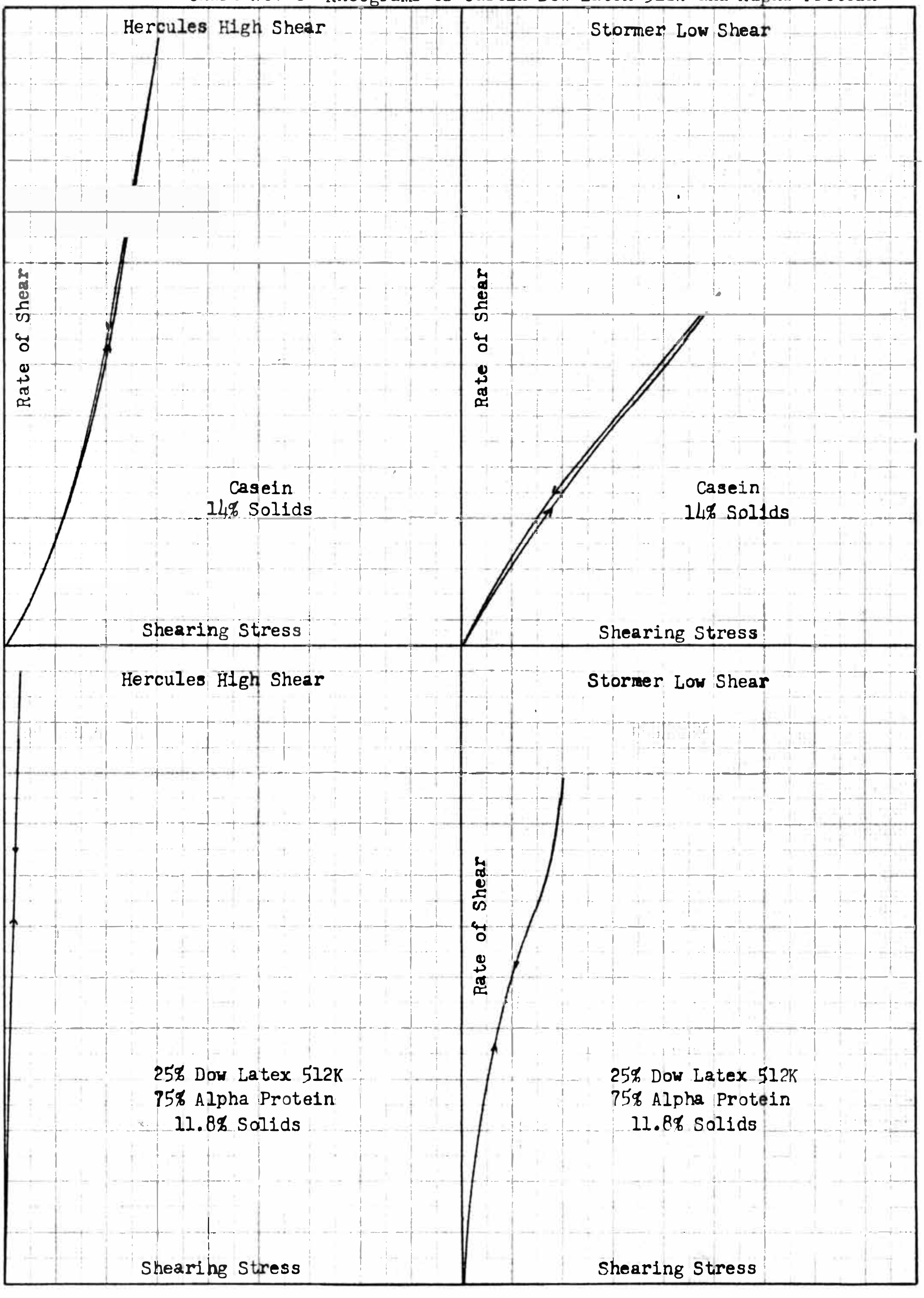


Chart No. 7 Rheograms of Dow Latex 512K and Alpha Protein

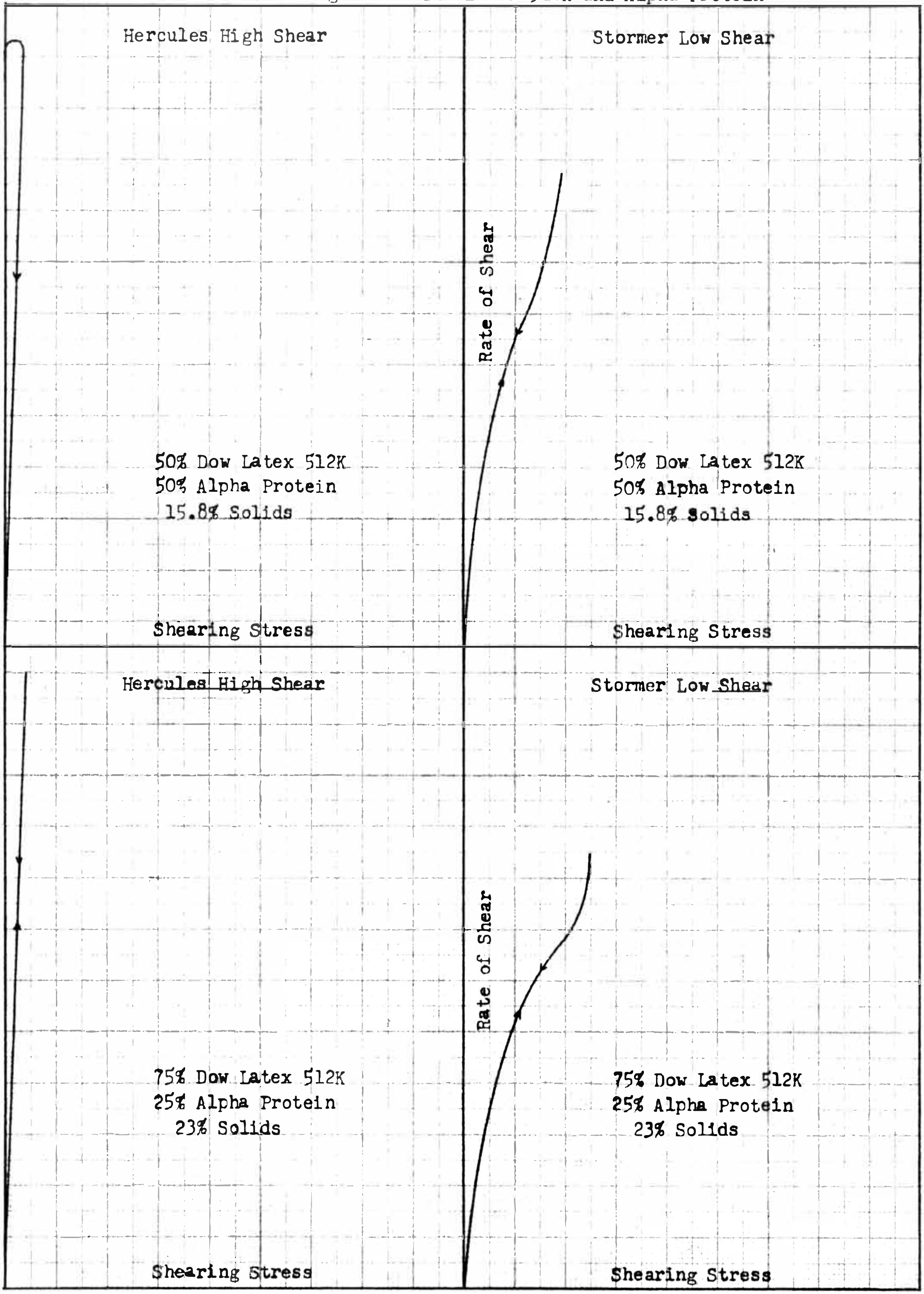


Chart No. 8 Rheograms of Clay and Dow Latex-Dow Latex and Alpha Protein

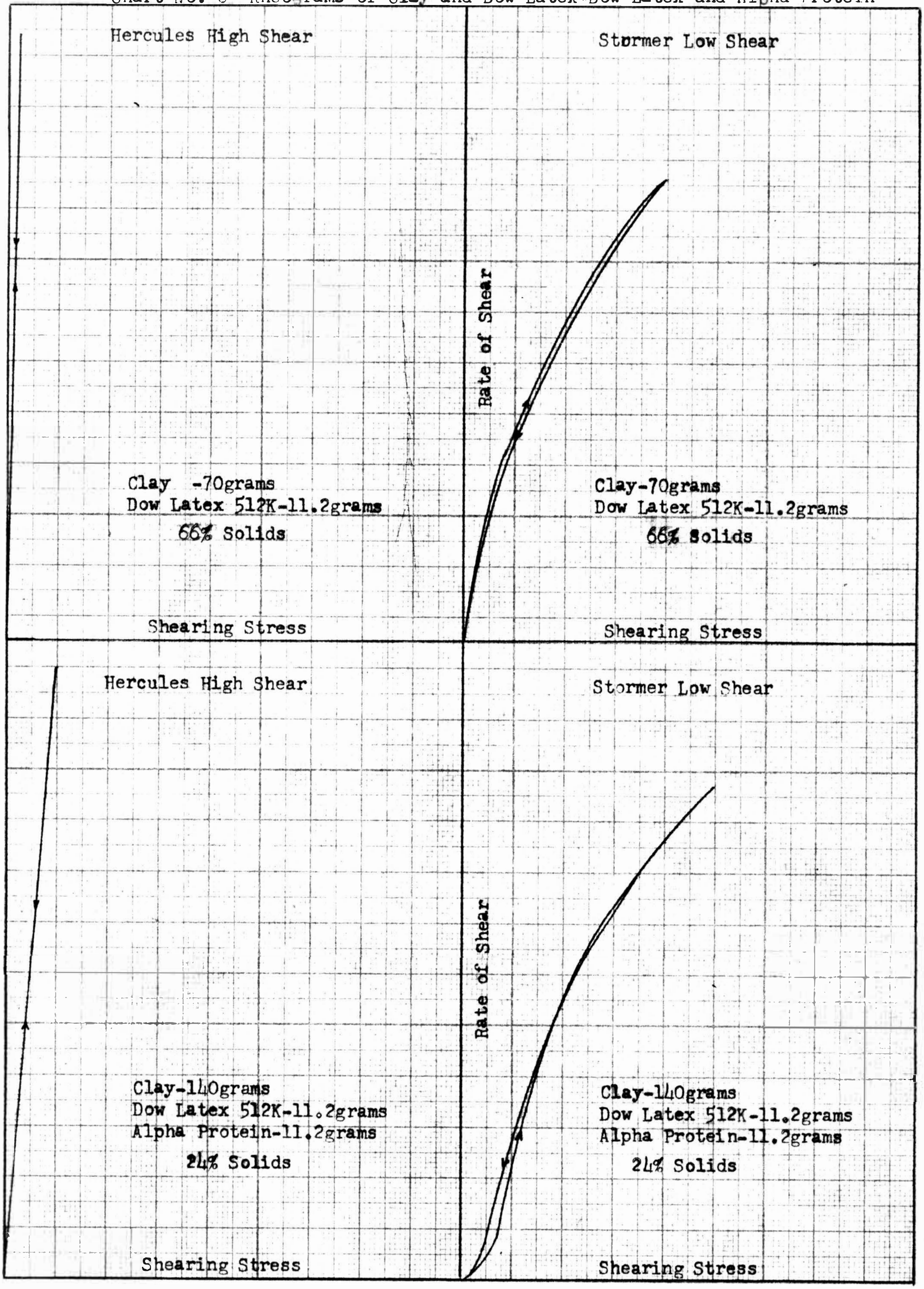
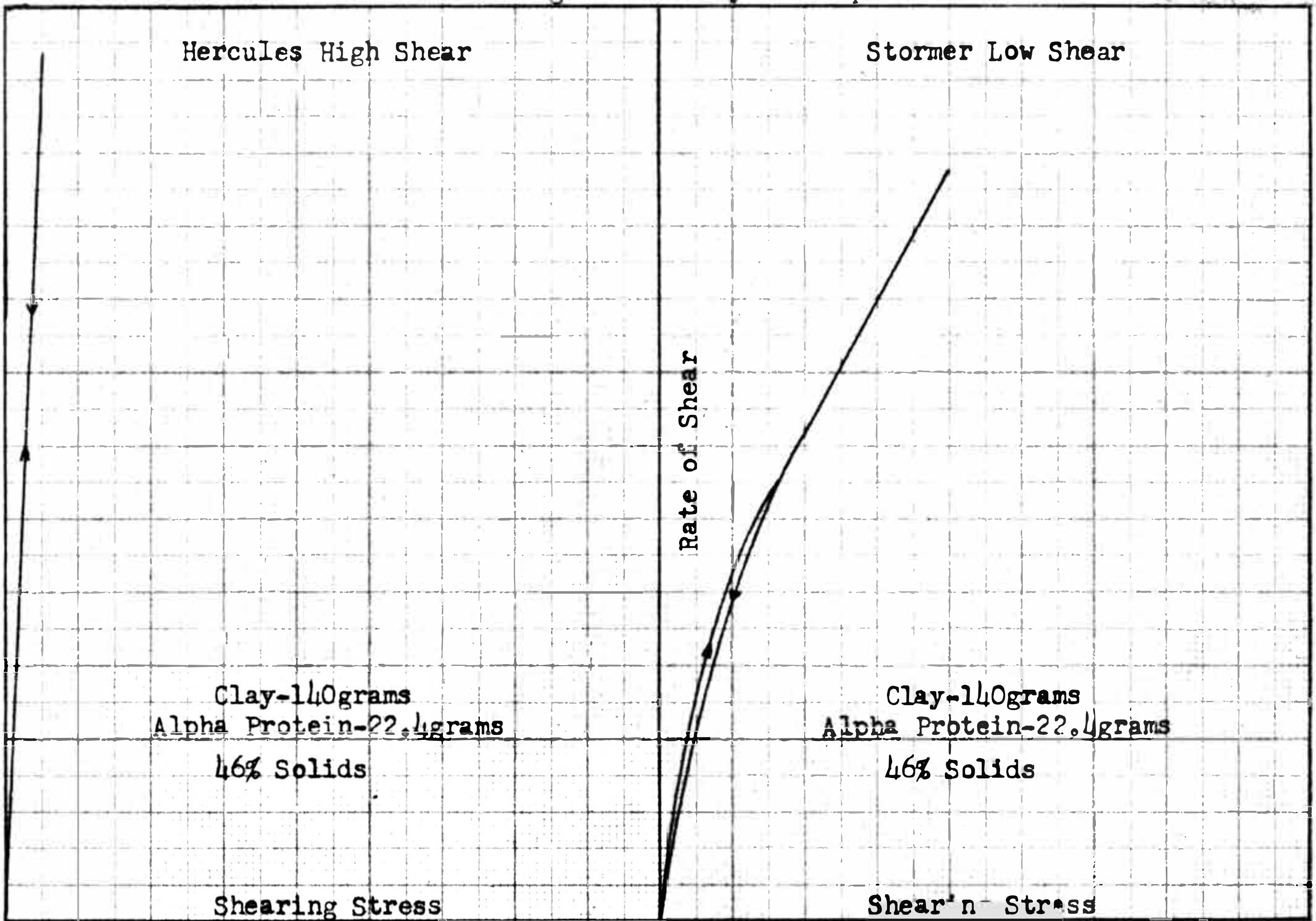


Chart No. 9 Rheograms of Clay and Alpha Protein



Literature Cited

1. Green, Henry, "Industrial Rheology and Rheological Structures", New York, John Wiley and Sons, Inc., 1949, 311 p.

2. Thompson, R. N., "Rheology in Paper Coating", Tappi Monograph Series No. 11, p. 43.

3. Dewey, Phillip H., "Rheology of Surface Coatings", Paper Mill News 70, No. 39: 114, 116, 118, 120-22, 124 (1947).

4. Applegate, Paul D., and Smith, J. Wilson, "The Hercules High-Shear Viscometer", Tappi, No. 31: 208-214 (1948).

5. Green, Henry, "How to Determine the Desirable Rheological Properties of Coatings", Paper Trade J. 125, No. 11: 49-53 (September 11, 1947).

6. Willets, William R., "The Rheology of Paper Coating", Tappi 33, No. 4: 261 (April, 1950).