1. The Concept

This was taken from Thomas M Riddick's book "Control of Colloid Stability through Zeta Potential". A link to a pdf copy of the entire book is available by email request.

The stability of a colloid system or emulsion is dependent upon adsorption of ions (or polymers) from the bulk of the suspending liquid. There are three present methods by which the colloid can be stabilized. In each, Zeta Potential reveals the actions and produces data which permit suitable adjustments to the stability of the system.

Substantially all colloids, both organic and inorganic, are electronegative when suspended in either distilled or tap water; that is to say, aqueous suspensions of low ionic concentration in the pH range of 5 to 10. Moreover, the Zeta Potential of such systems generally ranges from about —14 to —30 millivolts. Proteins also fall into this category, but they become less electronegative with decreasing pH, and their pH-ZP curves generally cross the line of zero charge in the pH range of 2 to 5.

Zeta Potential values less negative than −14 millivolts usually represent the onset of agglomeration. A plateau region, marking the threshold of either coagulation or dispersion, exists from about −14 mv to −30 mv. Values more electronegative than −30 mv generally represent sufficient mutual repulsion to result in stability. However, to *assure* stability with a "reasonable" factor of safety, Zeta Potential should be increased preferably to the range of say —45 to —70 mv.

One cannot categorically state that a colloid will or will not be stable at a given Zeta Potential, particularly in the delicately poised range of —15 to −30 mv, but certain broad generalizations may be made. The writer's experience with anionically dispersed systems, based on the Helmholtz-Smoluchowski formula (employed throughout this book), is:

TABLE NO. 1

Stability Characteristics	*Avg. ZP in millivolts*
Maximum agglomeration and precipitation....	0 to +3
Range of strong agglomeration and precipitation	+5 to −5
Threshold of agglomeration	−10 to −15
Threshold of delicate dispersion.....	−16 to −30
Moderate stability	−31 to −40
Fairly good stability	−41 to −60
Very good stability	−61 to −80
Extremely good stability	−81 to −100

A possible *electropositive* range of dispersion of zero to at least +70 mv is possible, but is seldom employed by either Nature or man.

At any given electronegative Zeta Potential from zero to about −15 mv, the degree of agglomeration can be markedly improved by also employing a suitable long-chain polymer to produce mechanical bridging.* However, at Zeta Potential values more electronegative than say −15 to −25 mv, true colloids (equal to or less than 1 micron size) in *dilute* suspension often fail to show any agglomeration upon the application of either an anionic or nonionic long-chain polymer. It will later be shown that certain *natural* systems (skimmed milk, for example) exhibit *absolute* dispersion at relatively low electronegative Zeta Potentials. This seems to be the result of Nature's nicely matching the dispersant with the colloid.

*LaMer and co-workers have dealt extensively with this phase, from both theoretical and practical aspects.

For *assured* stability, each colloid must retain its complete discreteness with *no* agglomeration. This discreteness may be achieved by:

a) Adsorption on the colloid of an anionic electrolyte or polyelectrolyte, to create strong mutual repulsion.

b) Adsorption of a strongly hydrated hydrophilic protective colloid such as gelatin, on a larger hydrophobic colloid. In this case, the affinity for water exceeds the mutual attraction of adjacent particles.

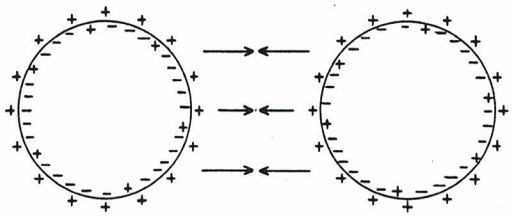
c) Adsorption of a nonionic polymer of sufficient chain length to create steric hindrance, to prevent two particles coming close enough to join. This method is widely employed for emulsions.

These three mechanisms are shown on Fig. 1.

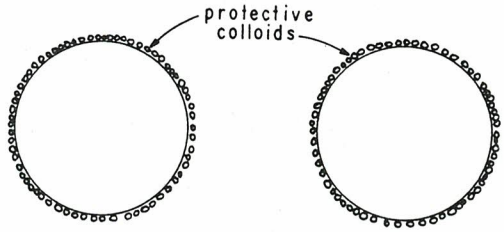
When coagulation is the desired end, Zeta Potential must be rendered less electronegative in order to reduce the forces of mutual repulsion. Gentle agitation will then create impingements of particles which enter the region where the short-range Van der Waals-London forces can furnish the attraction required to cause agglomeration. Optimum coagulation usually occurs in the Zeta Potential range of 0 to +3 mv.* Massive agglomeration is aided by employing a long-chain polymer to provide mechanical bridging, in addition to Zeta Potential control.

*In complex systems, it is occasionally possible to have maximum coagulation occur at Zeta Potential values outside this range. However, such cases are isolated, and the cause generally can be rationalized.

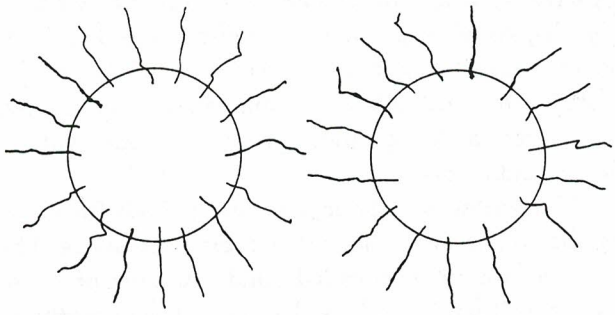
THREE METHODS FOR OBTAINING COLLOID STABILITY



METHOD 1: Mutual repulsion due to high Zeta Potential



METHOD 2: Adsorption of a small lyophilic colloid on a larger electronegative colloid



METHOD 3: Steric hindrance due to adsorption of an oriented nonionic polyelectrolyte

FIGURE 1

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2. Viewing the colloid

Much valuable information concerning the stability of a system can be readily gained through properly viewing the colloid. For example, when a high degree of dispersion is the desired end, a brief microscopical examination readily establishes the existence of even slight agglomeration. Conversely, the degree of coagulation of any system will be plainly indicated.

The writer has developed four methods for viewing the colloid with the stereoscopic microscope. The first two are for suspended solids systems of 10 to 1000 ppm (mg/l), and the last two for concentrated systems of 1 to even 70%. All are dark-field techniques, employing intense indirect illumination. Actually, one sees artifacts in the form of tiny specks of light reflected by the colloid. The compound microscope cannot be employed because its close working distance from objective to object permits direct light to enter the lens system. Procedures employing the Zeta-Meter stereoscopic microscope, ocular micrometer, and mirrored electrophoresis cell holder are shown on Fig. 2, and described as follows:

a) *Flat Drop Method* — A single drop of the (dilute) colloid suspension is placed on the surface of the glass cell holder as shown. The glass should first be washed with detergent, and wiped dry with a lintless towel so the drop will lie flat. Colloids having good reflective properties give the appearance of stars at night. Even slight agglomeration is clearly evident. Colloid concentrations as high as 1% may sometimes be viewed, but only at the edge of the drop.

b) *Raised Drop Method* — This technique is similar to "a" except that the glass surface of the cell holder should be dressed with silicone,* and *five* drops of the dilute suspension are employed to build up one large drop. This effect also can be obtained by forming the drop on a silicone-treated glass slide, which is then placed on the cell holder. The siliconed surface produces a depth-of-drop of about 3 mm as compared with less than 1 mm for the "flat drop" method. By viewing the drop at mid-depth, the glass surface of the cell holder disappears from view.

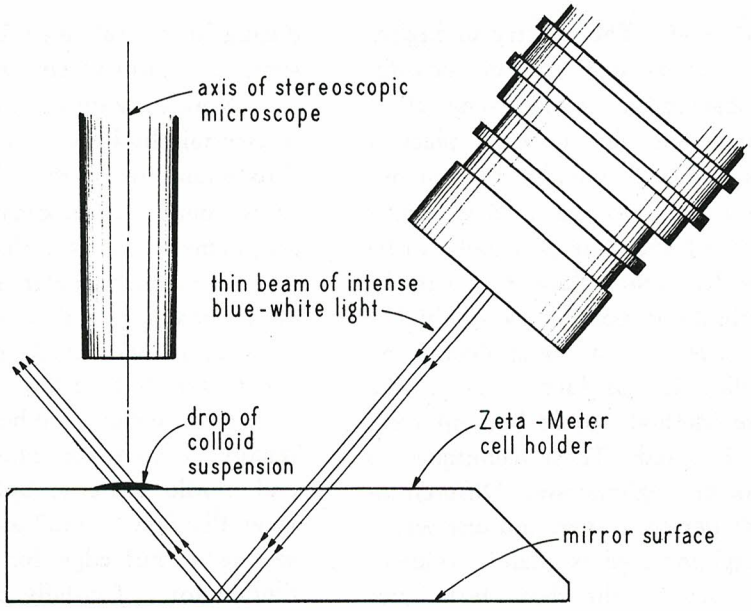
The "b" technique also enables one to estimate the number of "visible colloids per ml" by counting the suspended particles in one rectangle, sixteen rectangles, or the entire visible circle of the Zeta-Meter ocular micrometer. This value is then *multiplied* by the appropriate conversion factor listed below, which takes into account the area of the field, the "depth of *visible* focus,"** and the employment of 15X eyepieces. Results are in terms of "visible colloids per ml" which usually represent particles larger than 0.3 micron, depending upon their reflective properties.

TABLE NO. 2
CONVERSION FACTORS

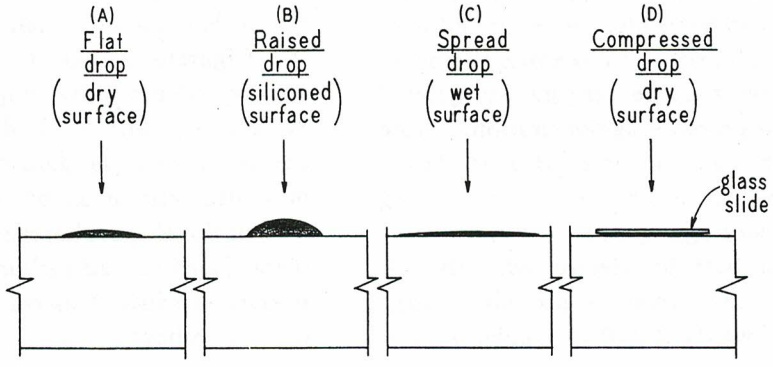
Objective	*One rectangular Micrometer field*	*All (sixteen) Micrometer fields*	*The Entire Circular field*
4X	40,000	2,600	210
6X	240,000	15,000	1,200
8X	460,000	30,000	2,500

*General Electric Company's "Drifilm" is suitable.

**"Depth of visible focus" includes all colloids which can be *seen*. In the electrophoresis cell, only colloids in *sharp focus* are tracked.



— Basic Method of Viewing the Colloid —



— Section through Cell-Holder showing Size and Shape of Drop —

FIGURE 2

The colloid concentration of slurries may be obtained by suitable dilution with Millipore-filtered* distilled water. A 0.22 micron filter should be employed and two passes are advisable to thoroughly clean the filter flask. The colloid concentration after dilution should not exceed 30 particles per single (rectangular) micrometer field. Unfiltered distilled water is not a suitable diluent because it usually contains 1,000 to 10,000 "visible colloids" per ml.

c) *Wet Plate Method*—To properly lower surface tension, the glass cell holder must be *freshly* washed with detergent, flushed copiously with tap water, and then with distilled water. The cell holder is drained on edge for a few seconds, then quickly placed on the microscope stage—and a small drop of the slurry applied from a height of a few inches. The drop immediately spreads on the water film to a diameter of 2 to 5 cm. This "thins" the liquid depth so that colloids may be readily viewed at the edge of the drop. This technique is applicable for colloid concentrations above 5%, and slurries of even 60% may be viewed to detect agglomeration.

*A product of Millipore Filter Corp., Bedford, Mass.

d) *Glass Slide Method* — The opacity of highly concentrated slurries prevents sufficient light passing through the drop to observe the colloid, except at its extreme edge. To overcome this opacity, place a single drop on the (dry) glass cell holder, then immediately cover it with a standard (75 x 25 x 1 mm) glass slide. The weight of the slide is usually sufficient to compress the drop and reduce it to a thickness where good visibility is possible. With highly concentrated systems, pressure may be applied to the slide to "thin" the film. If this fails to reveal the colloid, the Wet Plate Method should be employed, using also a pre-wet glass slide. These techniques do not significantly break up agglomerates. Differentiation between a well-dispersed system and one which has even partially agglomerated is plainly evident.

If colloid suspensions for the above techniques are prepared from *dry* powders, there is a decided tendency for materials to remain caked. This is because the repelling force of even strong electronegative Zeta Potential is insufficient to disrupt such aggregates. Therefore it is preferable to prepare colloid suspensions in a Waring blender or colloid mill, and to shear *prepared* slurries of unknown character. The slurry should thereafter be very gently agitated for a few minutes to promote agglomeration, before microscopical examination. However, if Zeta Potential is above −35 to −45 mv, no amount of stirring will generally form *any* aggregates.

The colloid can best be viewed with the 8X objective which, with 15X eyepieces, provides a magnification of 120X. Twenty-X (20X) eyepieces, producing an overall magnification of 160X, are occasionally helpful when viewing very fine colloids.

Working with an unknown colloid, it is helpful to ascertain both its average size and its size-variation throughout the system. The size of the colloid may be reasonably approximated by comparing its apparent diameter with the *thickness* of the ruled lines on the Zeta-Meter ocular micrometer. This thickness approximates 1.2 microns with the 6X objective, and 1.0 microns with the 8X objective. Usually, the *upper tips* of the vertical lines are employed for reference.

The viewing methods outlined permit one to readily differentiate spheres, plates, rods or needles, and motile bacteria. Spheres remain constantly in view. Platelets "blink" as they rotate and periodically expose a thin edge for light reflection. When the illuminator is *frontally* placed, needles appear to be oriented only in a left-to-right direction. If the illuminator is then positioned on the left or right, only the "vertical" needles will be "seen." Highly motile bacteria are very evident. Many types of bacilli rotate, and they appear alternately bright and dim as first their sides—and then their rounded ends—are reflected.

Cigarette smoke in *dilute* concentration can be readily examined by employing a glass ring about ¾" diameter and ¼" high, set on the cell holder and covered with a standard glass slide. It is perhaps the most dramatic of all Brownian Motion examples.

In the electrophoresis cell, overvoltage will cause plates (such as lead carbonate or crushed Pyrex glass) to dart like fish. This condition is relieved by reducing the voltage.

3. Photographing the colloid

It is impossible to reproduce photographically the colloid with the degree of visual clarity obtainable with the microscope. This is because the monocular lens "sees" the colloid only in a flat plane—as contrasted with *stereoscopic* viewing. Moreover, total magnification by the presently available camera and 8X objective is only 80X, as compared with 120X when one views the colloid. However, it is possible to obtain photographs which are at least informative, employing the stereoscopic microscope and the viewing techniques previously outlined. Light intensity must be raised (for a few moments) to maximum. The jack-knife illuminator, employing reflected beam illumination, must be brought to *sharp* focus and positioned *as close* to the liquid sample as possible. Shutter speeds must be precise and often require two to three trial exposures. This favors Polaroid-Land 15-second film. The most suitable camera assembly known to the writer is that produced by Paul Rosenthal.* The camera can be set in place by removing one eyepiece, and, in a period of only a few minutes, several exposures can be made and developed.

The "Flat Drop" method (a) produces good results, particularly after the drop has been permitted to stand for ten minutes. This results in some settlement and reduces Brownian motion. The imperfections in the glass surface of the cell holder are indistinguishable from colloids in the photograph, but this effect is not disturbing.

The "Raised Drop" (b) is often difficult to photograph because of particle movement. This can be reduced by shielding the drop from air currents with a 1" diameter plastic shield about 1" high.

Both the "Wet Plate" (c), and "Glass Slide" (d) methods give informative data on agglomeration.

The photographs which follow demonstrate varying degrees of stability in a number of colloid systems.

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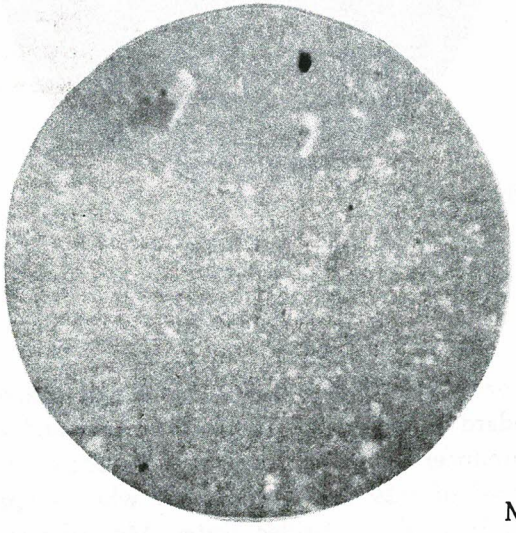
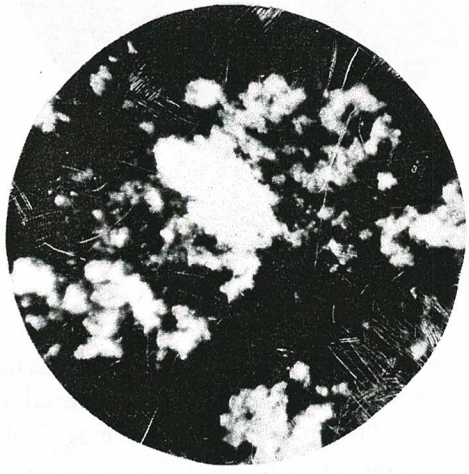
*This is known as the Romicron, and consists of a B & L type N camera fitted with a special Polaroid back. Film size is 3¼" x 4¼". 10X or 20X lenses are available, giving magnification of 40 or 80X with the 8X objective. This is equivalent to the microscope objective times the lens power of the camera, divided by 2. (Pictured on p. 108—Available from Paul Rosenthal, 300 Northern Blvd., Great Neck, N. Y.)



The colloid system before coagulation—
Zeta Potential —22 mv

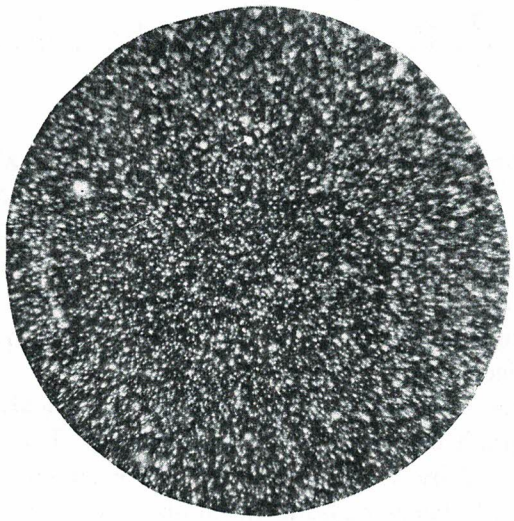
OVERALL
MAGNIFICATION
50X



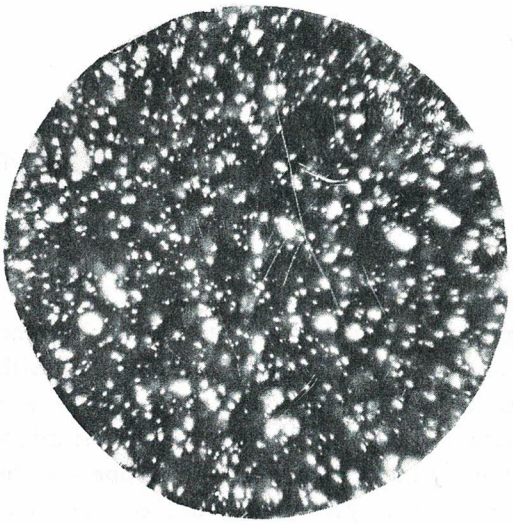
The same system after coagulation—
Zeta Potential, zero mv

FIGURE 3

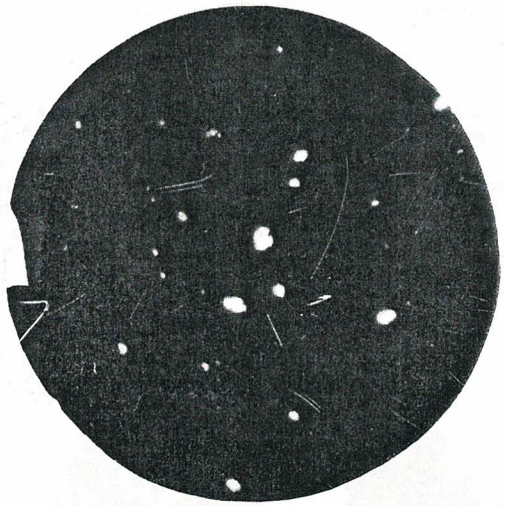
Coagulation of an aqueous system containing 1000 ppm colloidal silica; 1000 ppm kaolin; 10 ml/l skim milk; 10 ml/l domestic sewage; and 25 ppm alkyl benzene sulfonate.



Nat. Silica (Minusil #5)
ZP —30 mv

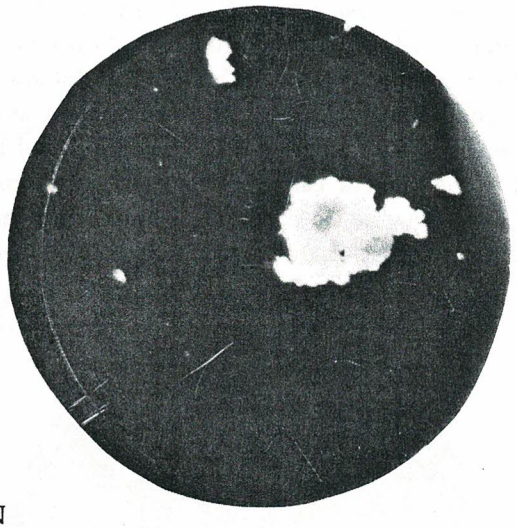


Nat. Silica
ZP —14 mv



Nat. Silica
ZP —6 mv

OVERALL
MAGNIFICATION
50X



Nat. Silica
ZP zero

FIGURE 4

These photomicrographs show increasing agglomeration with decreasing Zeta Potential for the colloidal silica "Minusil." Comparable agglomeration obtains for substantially all colloids which readily adsorb a cationic electrolyte or polyelectrolyte.

This silica is produced by Pennsylvania Glass Sand Corporation.* It is termed "Minusil—5 micron," and is a natural air-floated silica produced by crushing sandstone. The "5 micron" is rather a misnomer and indicates that it is in this *general* size range. Actually, according to Kane, LaMer and Linford,** its average diameter closely approximates 1.1 microns. The writer has used it for a number of years as a "standard test colloid." It adsorbs well, and all of the producer's samples thus far have shown a Zeta Potential of −29 mv ±1 or 2 mv when suspended (say 100 ppm) in distilled water. Minusil has been extensively employed as a test colloid in the systems presented herein. In all instances where this silica is mentioned, it refers to "Minusil—5 micron."

*Address: 375 Park Ave., New York, N. Y.; and Pittsburgh, Pa.

**Filtration and Electrophoretic Mobility Studies of Flocculated Silica Suspensions—J.A.C.S. 86, 3450 (1964).

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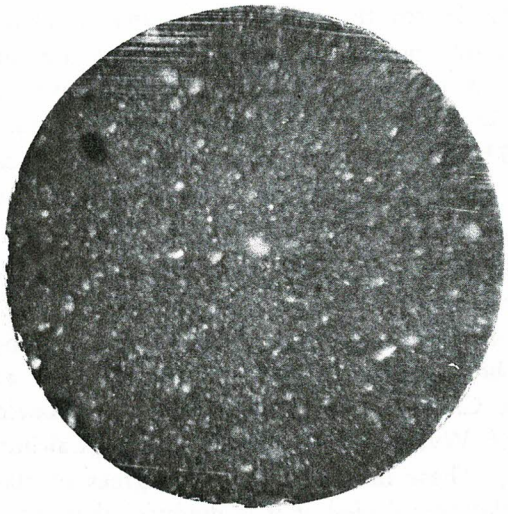
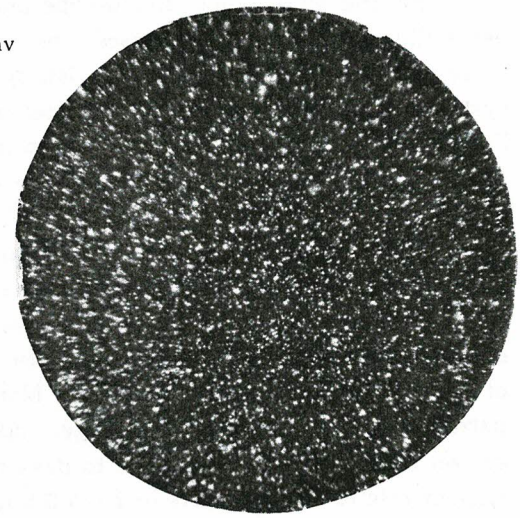
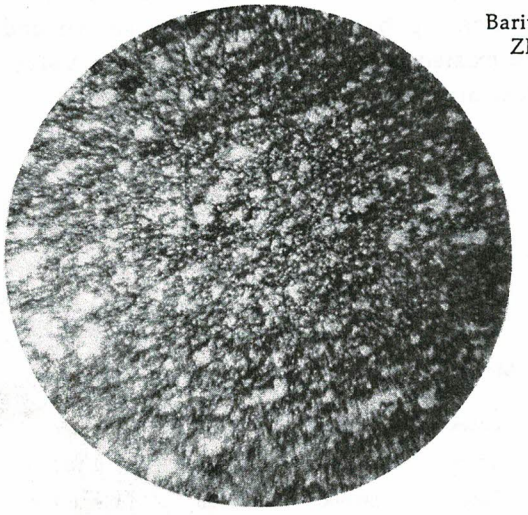


Bentonite
ZP −14 mv

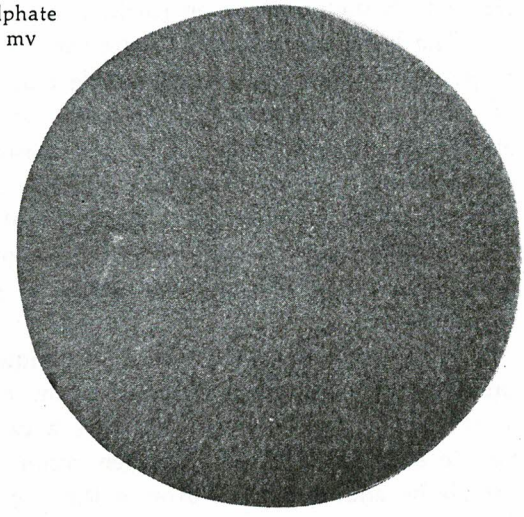
Bentonite
ZP −65 mv

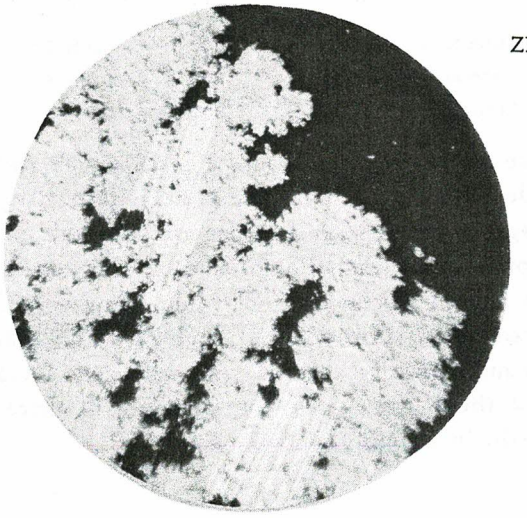




Barium Sulphate
ZP −15 mv

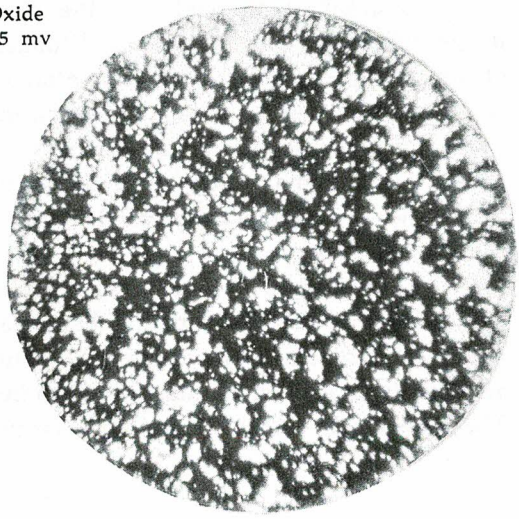
Barium Sulphate
ZP −80 mv





Kaolin
ZP −10 mv

Zinc Oxide
ZP −15 mv



OVERALL
MAGNIFICATION
50X

FIGURE 5

The photomicrographs for Bentonite and Barium Sulphate show dilute colloid systems in distilled water before and after anionic dispersion.

The Kaolin has been reduced in ZP from −22 to −10 mv by the addition of aluminum sulphate. The zinc oxide (CP, reagent grade) suspended in distilled water was slightly past the threshold of coagulation.

With the stereoscopic microscope and reflected beam illumination, one can assess the general stability (but not the detail characteristics) of colloid systems about 0.3 microns in diameter and larger. For details, we must rely on the electron microscope, which clearly shows the size and shape of discrete particles.

Particles in the size range of say 0.3 to 2 microns, which under the stereoscopic microscope *appear* discrete, actually may consist of agglomerates of smaller discrete particles which have joined to form aggregates of fairly uniform diameter. Apparently Nature abhors particles in the 200 to 2000Å range, and it is well known that in a matter of hours to days these often agglomerate to form clusters of from 0.5 to 1 micron size, which then enlarge no further.

The human eye, aided by the compound microscope at say 2000X, does not enable true resolution of particles (or contrasting surfaces) smaller than about 0.2 microns. This represents one-half wavelength at the start of the visible spectrum (400 millimicrons). The stereoscopic microscope at 120X or 160X enables one to "see" the outline of particles of this approximate size only by virtue of strong reflected light.

It is factual that with proper technique, colloids under the stereoscopic microscope appear in their *true* state of stability. If one centrifuges a calcium carbonate slurry at high G and then *reconstitutes* the sample by adding a small drop of the original slurry to the supernatant, the colloid is thereby suspended in its *original* mother liquor and undergoes little or no change in either Zeta Potential or stability characteristics. Thus, a colloid appearing discrete under the stereoscopic microscope will also be discrete in the original slurry. And similarly, a sample which shows agglomeration will be agglomerated in the original slurry.

The advantages of the electron microscope are tremendous, because they permit high magnification with sustained resolution and clarity. But there are also disadvantages which must be taken into account. The desiccation inherent to employment of high vacuum can destroy the structure of many organics; and also many inorganics such as hydrous iron or aluminum oxides. Moreover, sample preparation may (and usually does) materially alter stability characteristics. Though one may place reliance on size and shape characteristics of particles revealed by the electron microscope, the writer places little or no reliance upon stability characteristics indicated by electron micrographs.

We present herewith six electron micrographs through the courtesy of Dr. Emanuel Kontos of Naugatuck Chemical Co. (Latex), and Dr. Donald Peppard of Wyandotte Chemicals Corp. (Calcium Carbonate). These illustrate varying degrees of stability *as photographed*—but it is doubtful that there is any relationship between stability as shown and that which existed in the original suspension. Values listed below are average and approximate:

TABLE NO. 3

Fig.	*Material*	*Initial Magnification*	*Small Discrete Particles—Angstroms*	*Typical medium sized agglomerates—Microns*
6	Latex	50,000	380	—
7	Latex	14,000	2,100	1 to 2
8	Latex	50,000	2,000	0.4 to 1.6
9	Purecal O	15,000	700	0.5 to 1.5
10	Purecal T	30,000	800	0.3 to 1
11	Purecal U	30,000	300	0.5 to 2

These photographs illustrate a point which will be considered in detail later. The point is that many mineral agglomerates such as those pictured will *not* be disrupted if the Zeta Potential of the system is raised to a high electronegative value. However, if such a system is *first* brought to a high Zeta Potential and *then* mechanically sheared with sufficient force to disrupt these aggregates, the system *will* thereafter remain in a highly disperse state.

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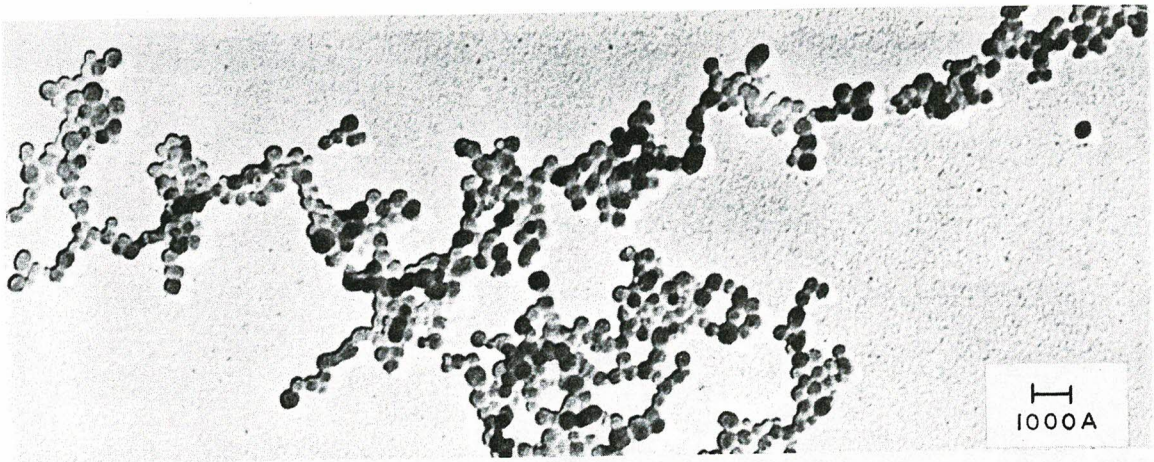

FIGURE 6

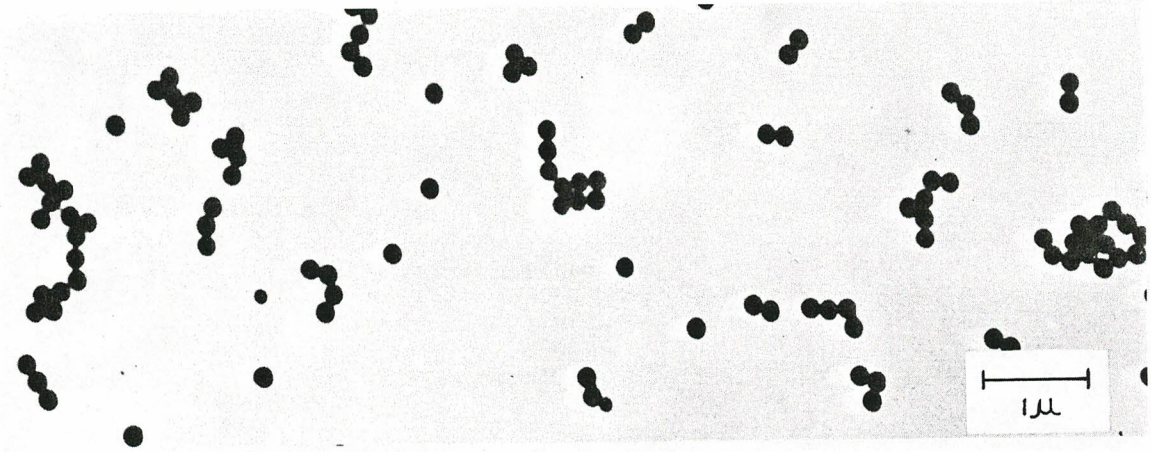

FIGURE 7

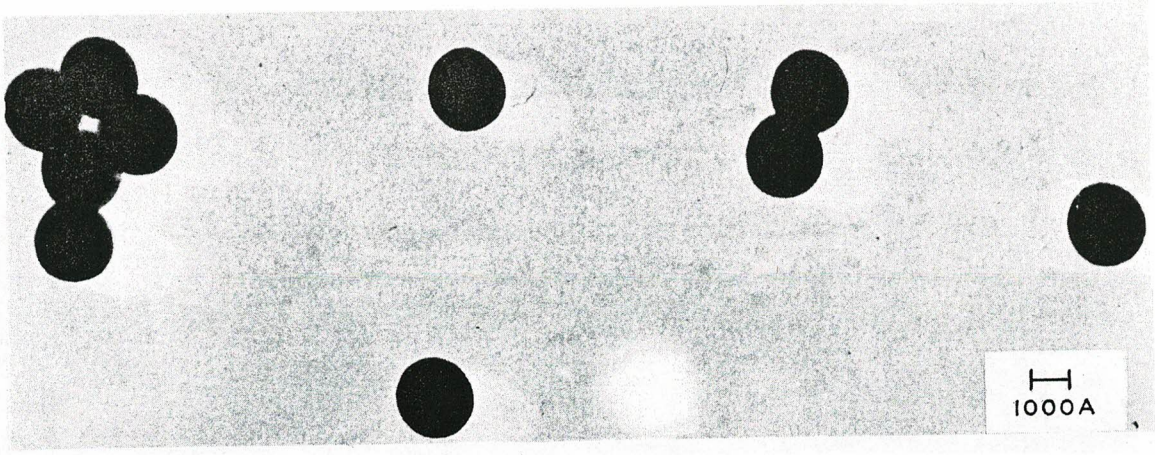

FIGURE 8

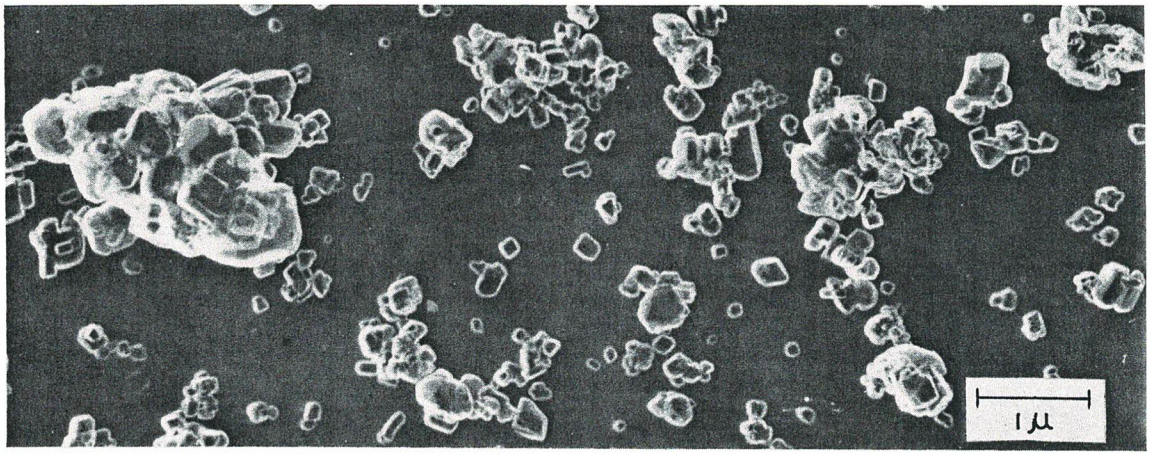

FIGURE 9

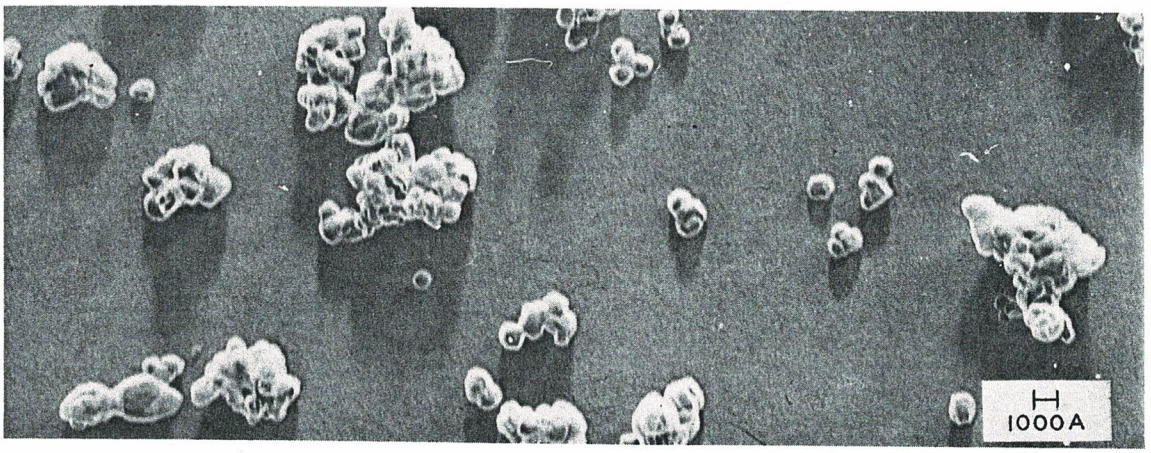

FIGURE 10

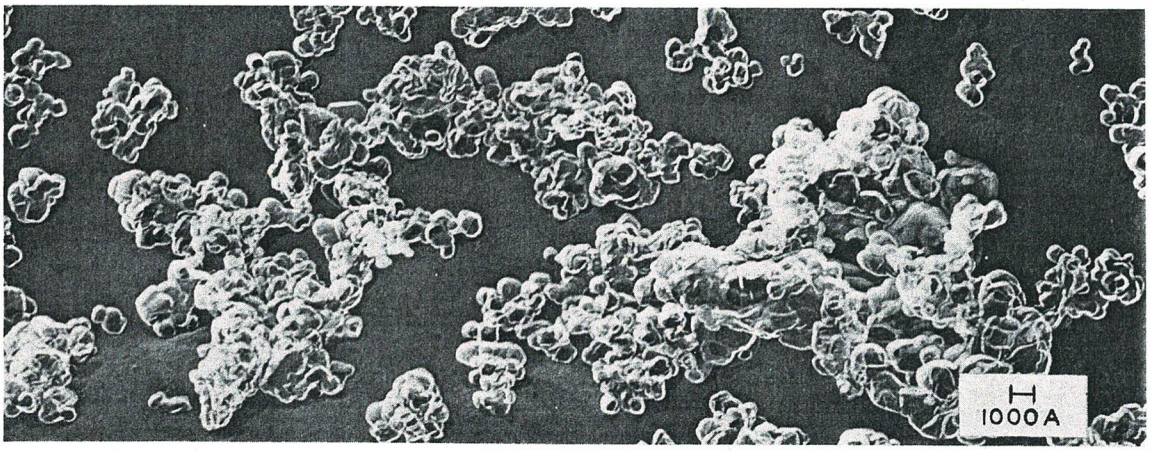

FIGURE 11

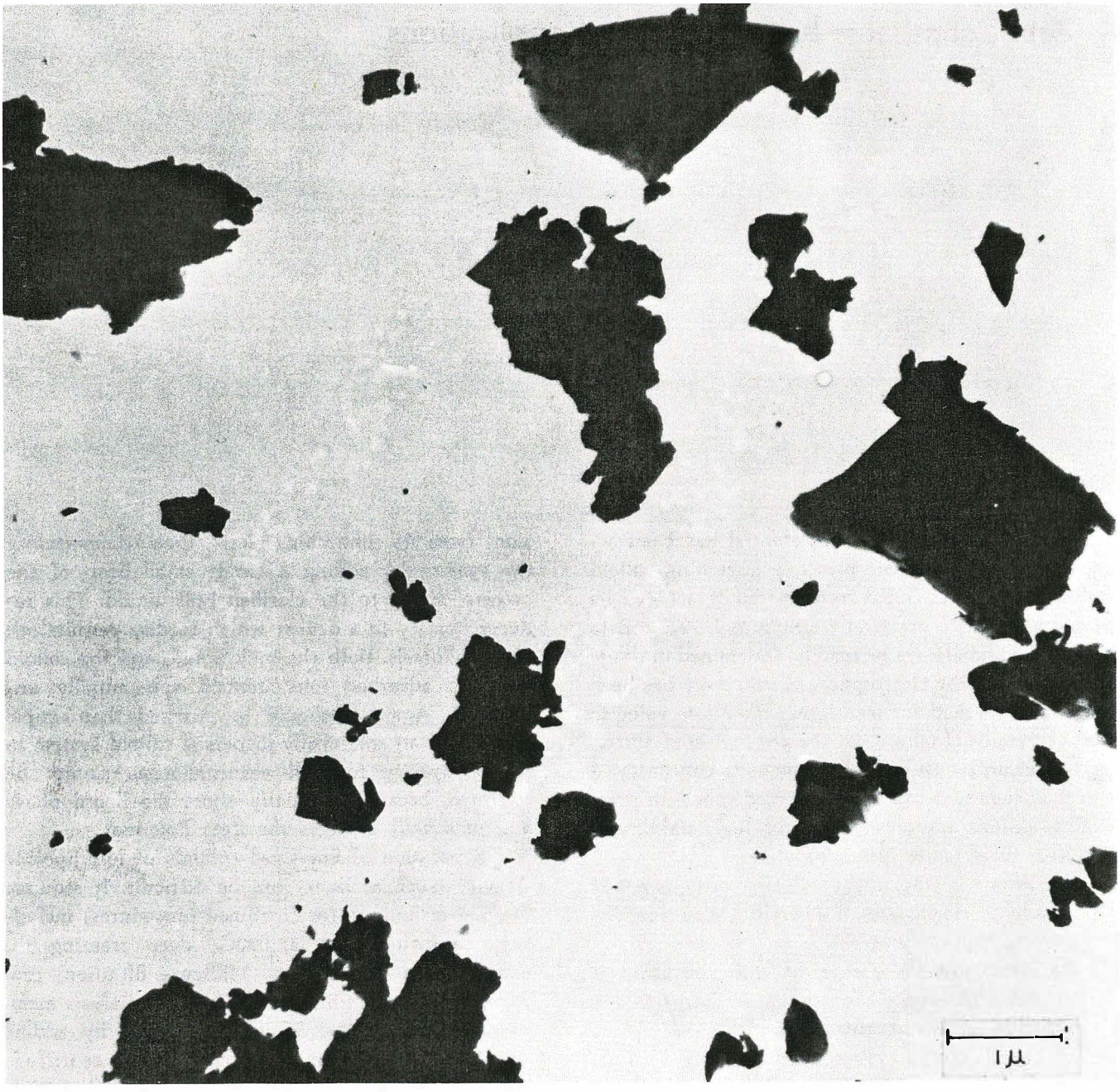

FIGURE 12

Fig. 12 shows an electron photomicrograph of Minusil (5 micron), an air-separated natural silica. As noted elsewhere, the "5 micron" is a misnomer, denoting maximum particle size. Actually, particle size was found by LaMer to average 1.1 microns, and size distribution is relatively narrow. Particles are angular and apparently rough in texture. The colloid adsorbs most surfactants quite well. In fact, the writer's coefficient of adsorption is based on Minusil.

In the writer's opinion, the particles shown are somewhat larger than typical. The material contains a very small percentage of two fine fractions, which are visually evident (at the top) when say a 60% suspension is centrifuged for 30 minutes at 37,000G. Surface area equals 2.06 square meters per gram.

It is difficult to find an organic test colloid of unvarying characteristics. For dilute suspensions, the writer often employs 5 ml/l of skim milk.