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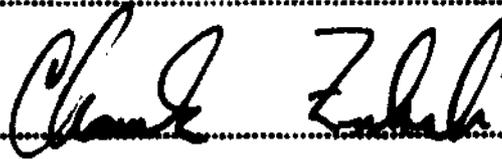THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Richard Y. Sugihara

ENTITLED The Surface Modification and Sintering of

Monodisperse Silica Particles

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF B.S. Chemical Engineering

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O-1364

THE SURFACE MODIFICATION AND SINTERING

OF

MONODISPERSE SILICA PARTICLES

BY

RICHARD Y. SUGIHARA

THESIS

for the

DEGREE OF BACHELOR OF SCIENCE

IN

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1. SUMMARY

This thesis investigates the particle surface modification of the colloidal silica in dispersion in order to verify existing results, describes developed laboratory techniques for particle modification, and studies the packing and sintering of this material.

The initial particle system was synthesized in a precipitation reaction involving tetraethylorthosilicate (TEOS), ammonia, and water in an ethanol solvent. The particles were modified via an esterification reaction with normal alcohols. The modified silica particles were then compacted in a hydraulic press and sintered.

The esterification reaction seemed to work and did not damage the shape nor the monodispersity of the initial particles. Laboratory techniques for esterifying the particles were simplified from the literature and, basically consisted of heating in an open beaker. The effect of the particle coating on the packing characteristics of the powder was increased cohesiveness, in comparison to the uncoated sample. Sintering of the mechanically-packed dry powder pellet revealed defects and cracking in both coated and uncoated samples. However, sintering took place at temperatures as low as 1200° C and with isothermal heating periods as short as 4 hours. In addition, less porosity was observed in the pellet made from coated silica.

2. INTRODUCTION

The development of ceramic materials is of special interest for many energy applications because of their potentially good mechanical properties at high temperatures and ability to withstand exposure to high temperature-hostile environments. [1] The problem that is hindering the progress of ceramic structure applications is its susceptibility to defects. Defects arise in the form of irregularities or inhomogeneities in the character of the bulk or surface of the structure. [2] The presence of defects in the microstructure forces designers and engineers to use property values in their designs considerably lower than the potential of the material in order to ensure almost absolute safety or integrity in critical and high cost devices because of the brittle nature of ceramic materials. This situation can be attributed to poor reliability and reproducibility of current ceramic processing. [1] Reliability and reproducibility essentially mean homogeneity and uniformity on a microscale from piece to piece and also on a macroscale. The achievement of homogeneity would reduce the scatter of property values and result in a higher effective value of strength for design purposes. It is obvious that good engineering practice and quality control during operation of specific machinery in the fabrication process are necessary to maintain homogeneity and uniformity. However, the nature of the response of the material(on an atomistic and particulate basis) [1] is equally important. This is the basis at which this project concentrates on. The goal of this project is to investigate ceramic structures fabricated from modified and unmodified monodisperse, spherical silica dioxide particles in colloidal suspension. This modification involves surface coating by esterification with normal alcohols.

3. SURVEY OF LITERATURE

Some previous works have been done on the formation of the silica particle dispersions, the coating by esterification with normal alcohols; and the packing and sintering of silica dioxide.

Particle Formation

The silica dispersion was produced by reacting tetraethylorthosilicate (TEOS) with ammonia and water in an ethanol medium. Two specific reactions occur to form the spherical particles. In the first reaction, the TEOS is hydrolyzed to silicic acid. This species undergoes a condensation polymerization reaction in which silicic acid molecules at supersaturated levels combine and eliminate water to produce the dispersion. Ammonia serves as a morphological catalyst by reacting with the silicic acid to produce its conjugate base. The resulting negative charge on the silica species creates a stable colloid due to electrostatic repulsion between the particles. [3] The condensation of silica from supersaturated silicic acid solutions has been found to be very dependent on the pH and the initial silicic acid concentration. It has also been determined that the temperature at which the reaction is run affects the size and the monodispersity of the particles. Several important trend have been discovered in experiments by Stober, Fink, and Bohn; and Van Helden, Jansen, and Vrij concerning the TEOS polymerization system. Trials have shown that the average particle size depends on the concentrations of water and ammonia in the reaction mixture. A detailed study of these relationships is found in a paper by Mark Tracy at the University of Illinois, Urbana. The size and mass fraction of these particles in solution can be increased by seeded growth. This growth can be accomplished by adding stoichiometric amounts of TEOS and water to the particle dispersion initially generated by the condensation reaction. These additions were made at eight hour intervals with constant stirring. The particles used in the modification step of this project were generated in a small scale four liter reactor that was designed and operated by Jeanne Chang at the University of Illinois, Urbana.

Surface Modification

Surface modification of these particles was also studied. An article by R.H.Ottewill describes the steric stabilization that occurs when particles are coated.The adsorbed layers modify the particle-particle interaction forces [4] as shown in Figure 1.From this qualitative illustration it is clear that the entry of particles by the presence of steric interactions. So in summary, the effect of particle surface coating is to increase the stability of the particles in solution. The surface modification that was done in this investigation was esterification with stearyl alcohol. This type of modification was described in an article by Van Helden, Jansen, and Vrij. It was chosen because this method seemed experimentally relatively easy. Specifically, it could easily be applied with the silica dispersions in alcohol, obtained by the Stober method. The Si-O-C bond, formed after esterification with a long chain alcohol, is chemically less stable than the Si-O-Si bond but, the stability is satisfactory with large organic groups and dense surface coverage. [5] The materials used for this synthesis were absolute ethanol, 14.2 molar ammonium hydroxide, TEOS, water, and stearyl alcohol. The TEOS was vacuum distilled to remove impurities. Characterization techniques were also discussed. They performed transmission electron microscope measurements with a Philips EM 301. Carrier grids covered with carbon-coated Parlodian films were dipped in a dilute dispersion and electron micrographs were taken of the particles that remained on the film. Light scattering studies, small-angle X-ray (SAXS) measurements, sedimentation velocity experiments, density measurements with a Precision Density Meter DMA 02C, and surface area determinations by physisorption of nitrogen with a Carlo-Erba sorptometric device were used to characterize the material. In addition, the carbon and hydrogen content of the silica was determined gravemetrically. The initial dispersions in alcohol

(alcosols) were prepared according to Stober's method. [6] whose reactions were briefly described earlier. His laboratory technique started with glassware cleaned with 2% hydrogen fluoride, and rinsed with both distilled water and absolute ethanol. Ammonium hydroxide, distilled water, and absolute ethanol were mixed in a reaction vessel. Then the TEOS was added and the reaction mix-

ture was stirred at ambient temperature for 18 hours. After an invisible hydrolytic reaction, in which silicic acid is formed, the condensation reaction of the supersaturated silicic acid was indicated by an increasing opalescence of the mixture starting one half to two hours after adding TEOS. No further change in turbidity was seen after 10 hours. The method of preparing coated silica by esterification of surface silanol groups with alcohols has been reported [7] to make the particles organophilic. A method by Iler involved adding a water-miscible alcohol to an aqueous silica sol and removing the water by distillation. Then the mostly water-free alcosol was heated to at least 100° C in order to make the esterification occur. In addition, Ballard showed that the degree of esterification increases with reaction time and temperature. He found that for stearyl alcohol, a dense layer of aliphatic chains is formed when the reaction is carried out at 200° C for 3 hours. VanHelden described a similar coating method. He effected esterification with higher alcohols by simply adding it to the alcosol and distilling off the lower alcohol. He indicated that it was preferred that the stearyl alcohol be added as a concentrated solution in ethanol. The amount of stearyl alcohol that was added was three to five times the silica weight. In the reaction, the silica changes from hydrophillic to hydrophobic and precautions must be taken to avoid irreversible aggregations of silica particles in this intermediate stage. This aggregation occurs by siloxane-bridge formation between different particles. It is important to keep the water concentration as low as possible just before the esterification reaction, because siloxane-bridge formation is retarded in a non-aqueous medium. The water concentration, in this method, was lowered at the beginning of the ethanol distillation to 4.4% by dilution with absolute ethanol in order to remove the water from the dispersion during the distillation process. Then the silica was esterified with stearyl alcohol at 180-200° C for three hours under a nitrogen atmosphere. The coated silica was readily dispersable in cyclohexane, n-alkanes, chloroform, and toluene. Stable dispersions were also obtained after esterification at 200° C for 40 minutes, and the stability did not change after lengthy heating (9 hours). Separation of the silica from the large excess of stearyl alcohol was done by a combination of vacuum/sedimentation or by a combination of nitrogen flow distillation/sedimentation or by sedimentation alone. In the nitrogen flow distillation, nitrogen gas

is blown over the stearyl alcohol melt containing the silica at 180° C. The stearyl alcohol vapor is carried along and crystallizes in the condenser. After distillation, the silica was dispersed in cyclohexane and sedimentated in an ultracentrifuge (18,000 rpm). When the purification is performed by sedimentation alone, the stearyl alcohol melt with silica was dissolved in a mixture of chloroform (60% by volume) and cyclohexane (40% by volume). Chloroform is used because it is a good solvent for stearyl alcohol. Cyclohexane is mixed in to increase the density difference of particle and medium, which increases sedimentation velocity. Two additional sedimentation runs in cyclohexane were done to remove all of the alcohol. When the organophilic silica was stored as concentrated dispersions in cyclohexane, the appearance did not change after more than two years. The coated silica can be dried for 24 hours under a nitrogen atmosphere without affecting its organophilic properties. Prolonged storage in air, however, diminishes its organophilic properties, most likely due to hydrolysis or oxidation of the coating layer. [5] Organophilic silicas can be characterized with many of the same techniques that were used for uncoated silica. Elemental analysis yields information about carbon content, which indicates the presence of stearyl chains on the surface of the particle. The surface area can be determined from the nitrogen adsorption study. Electron microscopy gives information on the size, shape, and the size distribution of the particles. Size information can also be analyzed with SAXS and dynamic light scattering methods. Sedimentation techniques allow the calculation of molar mass and the specific volume of the particle. Static light scattering studies yield information about the dispersion density and the particle interactions. The results of all of these analyses help characterize the particle structure. From the carbon content, the weight percentage of stearyl chains may be calculated, assuming that all carbon originates from stearyl chains. The associated hydrogen is then calculated and subtracted off from the percent hydrogen found in the elemental analysis. The remaining hydrogen is attributed to water present as silanol and water trapped in the particles during their preparation. The percentage of silica is calculated from the silicon content. The density of the silica core can be calculated from the density of the total particle and of the layer and the weight percentage of the layer. The density of the silica core tends to decrease as the diameter of the particle increases. The significant water content, low

density, and low refractive index indicate an amorphous silica structure. This is also confirmed by particle shrinkage in electron microscopy. Her suggested that the silica particles were formed by uniform aggregations of smaller ultimate particles less than 5 nm in size. [7] This hypothesis was verified by Van Helden in his SAXS experiments which showed ultramicroporosity. McMillan found that the porosity of inner and outer regions of the particle could be altered depending on the reaction conditions. Newly made particles formed at 25° C were very porous to nitrogen. After heating at 90° C the area determined with nitrogen greatly decreased. However, in both cases the area determined with -OH ions was the same. These results indicated that the peripheral pore sizes were decreased by the heating so that the nitrogen could not penetrate. By heating the dispersion for a while at pH 10, the pores closed some more and trapped water inside. At the outside edges of the particle, the water can escape and leave a compact silica structure. At the interior of relatively large particles, however, this escape is difficult. As a result, the mean density of larger particles is lower, and the density variation is greater. During the coating reaction the charge density sharply decreases because ammonia is evaporated and the particles are brought into a much less polar medium. When the coated material is redispersed into aliphatic solvents the electrostatic repulsion again dominates the particle-particle interactions because a little charge in these solvents can produce a sizeable potential, which is hardly screened due to the low concentration of ions.

Packing and Sintering

In order to achieve reliability and reproducibility in ceramic processing, uniformly packed green microstructures must be consolidated. [8] Uniform particle packing, produced from a stable dispersion of uniform sized powder, not only influences sinterability, but also results in uniform, controlled shrinkages. Although these concepts have been found to be valid for titanium dioxide, difficulties remain for general applications, mostly because of a lack of understanding of the phenomena that occur during the final processing steps. As a specific example, when dispersed sediments or casts are dried, non-uniform shrinkages result in fractures within the compact, which causes a loss of structural integrity upon sintering. An explanation for this type of behavior

hypothesizes that the problem arises from the separation (by design) of particles in the dispersed sediment resulting from the repulsive interparticle forces. Therefore, the volume of the sediment is defined by the average interparticle separation. As solvent is removed from the cast, particle adhesion to the walls and non-uniform drying result in tensile stresses large enough to overcome van der Waals forces, and cause cracks in the dried body. To eliminate the cracking problem, external forces such as chemical, electrical, or mechanical must be applied to overcome the repulsive electrostatic forces and collapse the dispersed sediment into a compact cast. This uniform reduction in cast volume leads to lower drying shrinkages and stresses, which reduces or eliminates cracking. Microdesigning of ceramic structures with submicron size particles requires total control over particle-particle interactions. [9] In dry powder methods of structure formation (mechanical press), this control is difficult or virtually impossible to achieve since submicron size powders in the dry state spontaneously agglomerate because of van der Waals attractive forces. These agglomerated powders result in poor mixing and packing density variations in the formed compact. Colloidal packing methods provide this desired control mechanism over particle-particle interactions. The removal of the suspending medium by a technique that does not alter the uniformity of the suspension can result in a uniform consolidation of the suspended particles. In addition, colloidal suspensions may be used to eliminate unwanted flaw origins, such as hard agglomerates and particles larger than a certain size, through sedimentation. Colloidal filtration is one method of consolidation. When a colloidal suspension is poured into a filtering mold, the suction of the liquid from the suspension results in the formation of a consolidated layer at the filter interface. During this filtration operation, the filtrate passes through two kinds of porous media, the consolidated layer and the filtration mold. The kinetics of the consolidated layer growth are expressed by: [9]

$$L_c = \frac{2\Sigma Pt}{k\eta(\alpha_c + \alpha_m)}$$

where L_c is the consolidated layer thickness; ΣP, the total driving force effecting filtration; η the viscosity of the filtrate; k, the constant resulting from a material balance; α_c and α_m, the average

specific porous medium resistances of the consolidated layer and the mold, respectively; and t, the filtration time. Because of the parabolic nature of the filtration process expressed in the equation above, the consolidation rate decreases with increasing filtration time. This rate decrease always limits the usefulness of the filtration route to a certain compact thickness. Processing the silica dispersions with this method generally result in bodies with very fine porosity (often from 2 to 10 nm) and high specific area (as high as 900 m^2/g). [10] Consequently, full densification is often achieved at lower temperatures (in the range of 700 to 1200° C). Processing involves washing the powders after precipitation with distilled water and drying. Then, the powders were calcined in an uncompacted arrangement for 24 hours at 200° C. · These powders were resuspended in distilled water using ultrasonification and pH adjustment (addition of ammonium hydroxide or hydrochloric acid). Green bodies were formed by allowing particles in suspension to settle slowly (under gravitational force) in plastic tubes. After complete settling, the supernatant liquid was drawn off and the disk-shaped compacts were dried under ambient conditions and removed from the tubes. Two-dimensional, close-packed hexagonal arrays of particles were observed in these compacts. [10]

4. APPARATUS

Various equipment set-ups were used in the different steps of material processing in this investigation.

Particle Formation

Initial particle formation was done on a bench-top scale. 100 ml volumes of particle dispersions were formed in 250 ml polyethylene bottles. Reaction mixtures were pipetted into these bottles and a magnetic stir bar was deposited inside. The bottle was capped and placed in a water bath on top of a stirring plate. The water was kept at a constant temperature by the heat/fluid pump (Allied-Signal). Seeded growth was carried out right in this same apparatus. Larger scale (4 liter) particle generation was done in a reactor designed and operated by Jeanne Chang.

Particle Esterification

Particle coating by esterification was accomplished in a 2 liter open beaker. The coloidal silica was transferred into the beaker along with the stir bar. The beaker was heated and stirred with the stir/heat plate (Corning). The temperature of the reaction mixture was constantly monitored with a thermometer supported by a ring stand and clamp arrangement.

Packing and Sintering

The processed, dry powder silica was packed with a hydraulic press. The compacts were sintered in a programmable furnace. Both pieces of equipment were located in the Ceramic Engineering building at the University of Illinois, Urbana.

5. PROCEDURE

Procedures for the various parts of the silica processing were either followed from the literature or modified.

Particle Formation

Laboratory techniques for forming the initial silica dispersion were taken from a report by Mark Tracy. [3] Before use, the reagents were properly prepared. Reagent grade TEOS (Fisher Co.) was distilled under a vacuum of 29 in. of mercury. The first and last 10% of distillate were discarded. Ammonia hydroxide was pre-titrated and was found to be 14.2 M. Absolute ethanol (U.S. Industrial Chemicals Co.) and deionized water were the other reagents used.

Before starting the reaction, the glass and plastic pieces of equipment were cleaned. Dirty items were rinsed with a 2% hydrofluoric solution to etch away silica residues. Then the equipment was rinsed with soapy water and followed by a rinse with distilled water. A final wash with absolute ethanol was done to insure that no residual water remained on the clean item.

After the glassware was clean and dried, the solutions were prepared. First, the appropriate amount of each reagent was calculated as shown in Appendix A. These calculations were based on concentration data found in Tracy's report. The calculated amount of ethanol solvent was first pipetted into the polyethylene bottle. Then the water was added, followed by the ammonia. The bottle was quickly sealed to minimize the escape of ammonia. Slow stirring of the solutions was started to mix the reagents. Finally, the TEOS was added. The reaction was run in a water bath at 25° C. A magnetic bar and stirring plate were used to provide constant agitation. Solutions were stirred for 20 hours to insure that the reaction was complete, although the first turbidity appeared in the mixture after about 30 minutes. Seeded growth was achieved by simply adding stoichiometric amounts of TEOS and water (2:1 moles water to TEOS) every 8 hours for 56 hours.

A copper Formvar-carbon coated grid was dipped into the dispersion to obtain a sample. Excess solution was absorbed off the grid by placing it on filter paper. Electron micrographs of the sample were then made. The magnification of most of the negatives were photographed at 17,000 to 60,000 X. Particle diameters could be obtained directly from the photographs. In addition, an FTIR analysis was performed on a dry powder sample of these particles in order to detect the presence of O-H vibrations in the silanol groups shown in Figure 2. Also, dry powder samples were submitted for elemental analysis of carbon, hydrogen, and silicon.

Particle Esterification

Particle esterification was done by placing 1 liter of the silica dispersion (alcosol) in a clean 2 liter beaker. The solution was first heated on a heating plate and absolute ethanol was periodically added in order to reduce the water concentration. Magnetic stirring was used to prevent violent bumping. The ethanol-water azeotrope behavior is illustrated in Figure 3 in the Appendix. Also, the theoretical amount of ethanol required to reach the azeotropic boiling point of the mixture can be calculated from the equations given in this illustration. After the azeotropic boiling point was reached (at 78.15° C) in about 1.5 hours, stearyl alcohol (Kodak) was introduced into the volume-reduced (about 50%) alcosol in the solid form (M.P. 60° C) The stearyl alcohol was periodically added while maintaining about 500 ml of reaction mixture. The mixture was heated to about 190° C for 1 hour. The coated silica was then purified by a sedimentation method. A mixture of 60% (by volume) chloroform and 40% cyclohexane was added to the silica-alcohol mesh in order to dissolve the stearyl alcohol. Then the solution was sedimentated in an ultracentrifuge (Beckman) at 3,000 rpm for 20 minutes. This cleaning process was repeated several times until stearyl alcohol was not visible in the supernatant. Its presence could be detected by allowing evaporation of a small quantity of the supernatant and observing the residue. A white,waxy substance indicates the presence of the stearyl alcohol. Silica, desired in the powder form, was processed by taking the sediment from centrifugation and drying it in an oven for 24 hours at 75° C. Otherwise, the silica was stored by resuspension in cyclohexane. An elemental analysis was performed on these dry,

modified particles for carbon, hydrogen, and silicon. Also, a FTIR analysis was done on the dry particles in order to check for the absence of O-H vibrations in the silanol groups that is caused by the replacement of the hydrogen by stearyl chains as shown in Figure 4. In order to learn about the weight loss behavior of the dry particle as a function of temperature, a thermogravemetric analysis was performed on the DuPont 3050 TGA and the 1080 microprocessor. This analyzer consisted of an electronic arm balance, furnace, and a microprocessor to control the heating schedules and store data. The procedure to operate this analyzer involved placing about 25 mg of sample in a pan on the end of the balance arm, electronically zeroing, and programming initial and final temperatures, heating rates, and time of isothermal heating. Aluminum pans were used at temperatures below 1000° C but, platinum pans had to be used at higher temperatures. These pans were crafted most economically from thin platinum foil.

Packing and Sintering

The dry powder was packed mechanically with a hydraulic press. The applied pressure was set on a dial and the powder was placed in a cylindrical cavity in the machine. Then a piston was lowered into the cavity and compacted the powder. Afterward, the piston was withdrawn and a rod under the cavity pushed the pellet up and out of the cavity.

The compacted pellets were then sintered in a programmable furnace at different heating schedules.

A final study was attempted by centrifuging some of the coated silica dispersion in order to get a sinterable pellet.

6. RESULTS

Particle Formation

The success of the formation of spherical, monodisperse particles was verified with micrographs of the samplings taken from the alcosol. These photographs are found in Figures 4 and 5. Magnifications of 17,000 and 60,000 X were taken. Figure 6 and 7 show the effect of reagent concentrations on particle size and monodispersity. Figure 6 shows the effect of an error in the amount of reagent added. The particles were smaller than expected and were not very monodisperse. Figure 7 shows polydispersity and bimodal particles. Figure 8 displays a micrograph taken at 170,000 X. It possibly shows evidence of the "ultimate particles" Iler said agglomerate to form the larger sphere. The effect of seeded growth is illustrated in Figures 9 and 10. Initial particles (Figure 10) were about 440 nm in diameter. After seeded growth, the particles were about 1000 nm in size.

The result of the FTIR analysis is found in Figure 11. The spectrum reveals a band at about 3250 wavenumbers. This peak, according to Sacks, [10] indicates the presence of silanol groups (Si-OH) on the particle surface.

The result of the elemental analysis is displayed in Figure 12. The clean silica powder was found to contain .15% carbon, .67% hydrogen, and 43.32% silicon.

Particle Esterification

Micrographs of the esterified product are found in Figures 13 and 14. The photos reveal that the technique that was used to effect the esterification did not adversely affect the monodispersity nor the shape of the silica particles. Resolution was not great enough to determine if there was an increase in particle diameter due to the surface coating.

The FTIR analysis displayed in Figure 15 showed no peak in the 3000-3400 wavenumber region. This absence provides strong evidence showing that there is less Si-OH present; and, instead, there is more $Si-OC_{18}H_{37}$ at the particle surface.

The results of the elemental analysis shown in Figure 16 further supports the success of the reaction. The carbon content in a dry sample of esterified particles was found to equal 3.85%, while the hydrogen was 1.15% and the silicon was 41.86%. This increase in carbon and hydrogen content indicates the presence of stearyl chains on the particles. From this data, the percent of hydrogen due to silanol and trapped water; and hydrogen due to the stearyl chains can be estimated as done in Appendix B. The hydrogen due to silanol and trapped water was found to be .0050%, while the hydrogen due to the stearyl chains was found to equal .0066%.

Thermogravemetric analyses were conducted and the results are displayed in Figures 17, 18, and 19. Different heating schedules and final temperatures were selected. All of the runs showed a significant decrease in weight (3.8%) in the temperature range of 400-600° C. probably due to the burning off of stearyl chains. This result roughly agrees with the literature value of 500° C cited by Iler. This value, 3.8%, also is in agreement with the results from the elemental analysis (3.65% carbon, .0066% hydrogen).

Packing and Sintering

The dry, unpacked powders of coated and uncoated silica are pictured in Figure 20. The uncoated powder appears white and fluffy. It is very fine. The coated particles appear white and somewhat clumpy. When each powder is blown on, the uncoated particles fly into the air in tiny bits, while the coated particles roll away in small chunks. Pellets of both types of powder were mechanically packed. Photographs of fractured pellets are found in Figure 21. Before fracture, each pellet had a diameter of 16 mm and a thickness of 4 mm. When the uncoated pellet was fractured, it broke into several pieces and revealed a grainy, grooved surface with irregular breaks. The fracture surface of the pellet made from coated silica was smooth and clean. The pellet broke into only two pieces.

The sintered pellets, done at various heating schedules, are pictured in Figures 22, 23, and 24. The heating schedules are illustrated in Figure 25. The compacts in Figure 22 were run up to 1000°

C. Neither pellet sintered, as indicated by their original white color. The uncoated pellet looked much like the initial compact. It fractured upon heating and revealed irregular surfaces, again. The coated pellet fractured into many pieces but, the surfaces were smooth. Both of the compacts run at 1200° C sintered, and are pictured in Figure 23. The diameter of each pellet was about 12mm and the thickness was about 2.8 mm. These numbers represent a 25% shrinkage in diameter and a 30% shrinkage in thickness. The uncoated compact did not fracture but, it showed a lot of porosity and defects. A white color was still evident. The coated pellet fractured into several pieces but, it did not show the porosity that was evident in the uncoated pellet. The pieces were transparent, which indicated a higher degree of sintering was achieved, in comparison to the uncoated pellet. The fracture surfaces were smooth. Pellets were also sintered at 1200° C with an isothermal heating plateau at 450° C for 1 hour (to burn off stearyl chains). The uncoated pellet appeared the same as the one that had no isothermal heating. The coated pellet still had cracks, but there were much fewer than in the first run. Both pellets were about the same size as the others sintered at 1200° C.

A final attempt was made at consolidating a pellet by sedimentation. A dispersion of the coated particles in cyclohexane was centrifuged at 6,000 rpm for 30 minutes. However, the pellet broke when it was removed from the test tube.

7. CONCLUSIONS

This investigation of ceramic structure processing has led to the following conclusions:

1. Generation of monodisperse, spherical colloids of silica dioxide is relatively easy to accomplish. It is also well defined in terms of reagent concentrations and the corresponding particle size formed.

2. The ester.fication of the silica spheres with stearyl alcohol is definitely possible as reported by Iler and Van Helden

3. Esterification does not destroy monodispersity or the shape of the silica particles.

4. The organophilic property of the coated silica allows it to to pack with improved cohesiveness, as compared to the uncoated material.

5. The stearyl coating serves as both a stabilizer in dispersion, and a binder in consolidation.

6. Mechanical packing of dry powder samples of precipitated silica dioxide (coated and uncoated) does not result in a homogeneous, uniformly consolidated compact.

7. Esterification with stearyl alcohol reduces the porosity in sintered silica dioxide pellets.

8. The presence of stearyl chains causes the compact to fracture upon sintering, under present conditions.

8. RECOMMENDATIONS

In order to answer questions raised from this study and to further investigate the ceramic structure processing from silica, much work can follow.

1. Different alcohols can be used to esterify the silica.

2. Different sizes of silica particles can be esterified.

3. Compact formation can be done by filtration techniques.

4. Compact formation can be tried with gravity sedimentation.

5. Compact formation techniques can be developed for ultracentrifugation. Possibly, after centrifugation, the supernatant could be drawn off and the fluid container and compact would be heated in an oven for a period of time. This might expand the container and slightly shrink the compact to allow easy removal.

6. A distillation apparatus could be designed to handle the esterification process and recover vaporized stearyl alcohol.

7. Pictures of fracture surfaces could be taken with the electron microscope to study the particle arrangements in the sintered and unsintered compacts. Also, coated and uncoated compacts could be compared.

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APPENDICES

DLVO

Schematic Potential-Energy Diagram For Steric Stabilized Particles

POTENTIAL ENERGY

Surface Separation Distance
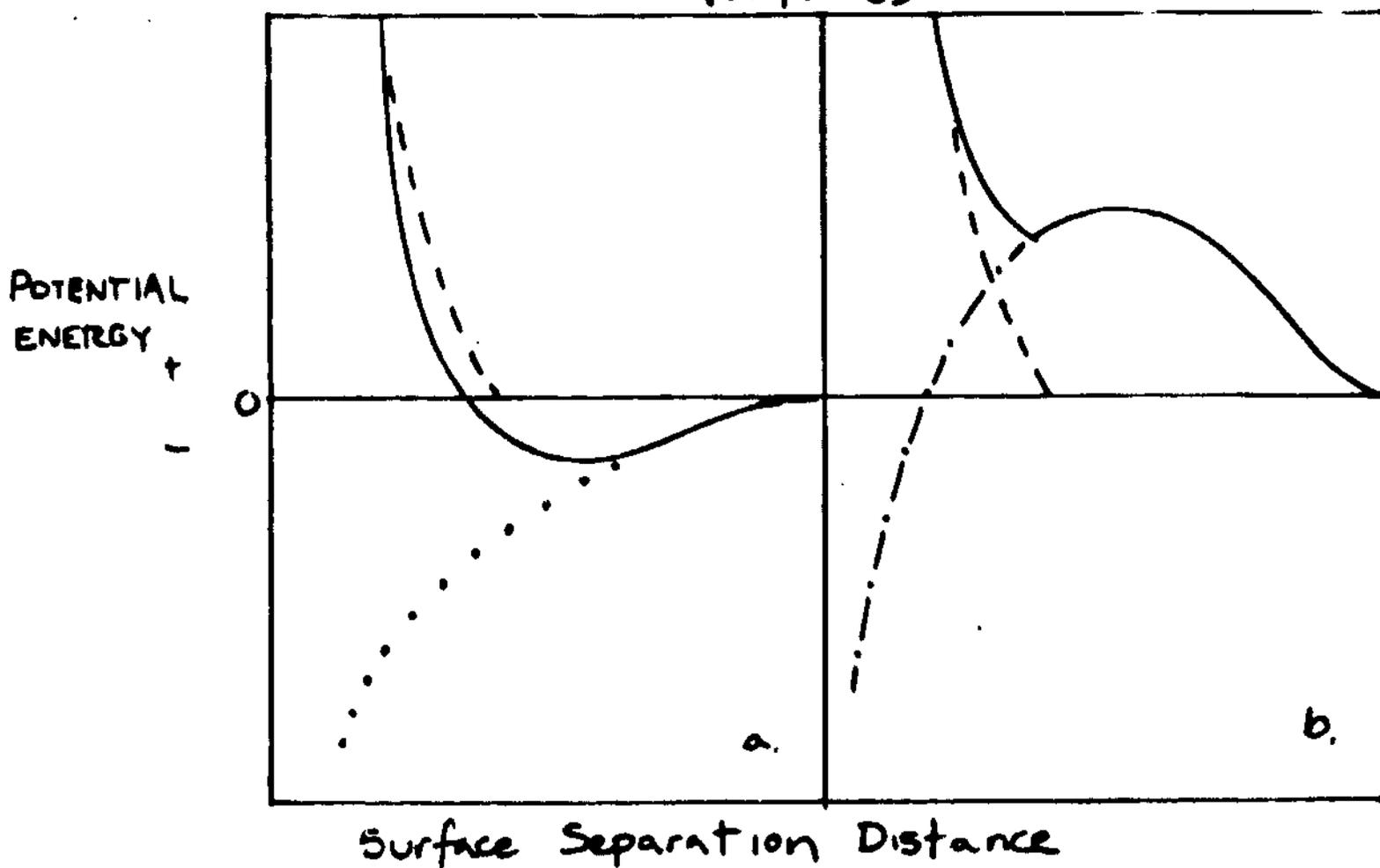
V_T = Total Potential Energy

V_R = Repulsion Potential

V_A = Attraction Potential

V_S = Steric Hinderance Interaction Energy

a.) Absence of electrostatic repulsion V_S - - -; V_A ·····;
V_T = $V_S + V_A$ ———.

b.) Presence of electrostatic repulsion V_S - - -;
$V_R + V_A$ —·—·—; V_T = $V_R + V_A + V_S$ ———.

Figure 1

Fig.¹

APPENDIX A

SAMPLE CALCULATIONS FOR PARTICLE FORMATION REAGENTS

(100ml total reaction volume)
(300 nm particles)

→ Amount of 14 M NH_4OH used to get 1.00 M NH_3

$$14 M \times \frac{X ml}{100 ml} = 1.00 M \quad , \quad X ml = \boxed{7.14 \; ml \; NH_4OH}$$

→ Moles of H_2O in NH_4OH added

14 M NH_4OH × 35.05 g/mol = 490.42 g/l , $\rho_{NH_4OH} = .9 g/ml = 900 g/l$

$$(900 \; g/l - 490.42 \; g/l) \times \frac{1 mol}{18.02 g} = 22.73 \; M \; H_2O \; in \; NH_4OH$$

$$22.73 \; M \; H_2O \times (7.14/1000 \; l) = .1623 \; mol \; H_2O$$

→ Moles of H_2O in 10.00M H_2O

$$10.00 \; M \times \frac{100}{1000} \; l = 1.00 \; mol \; H_2O$$

→ Moles H_2O to be added

$$(1.00 - .1623) \; mol = .8377 \; mol \; H_2O$$

$$.8377 \; mol \times \frac{18.02 g}{mol} \times \frac{ml}{1.00 g} = \boxed{15.10 \; ml \; H_2O}$$

→ Amount of TEOS required

$$.17 M = \frac{X ml \times \rho_{TEOS} \times MW_{TEOS}}{Total \; Volume}$$

$$= \frac{X ml \times .932 \; g/ml \times \frac{mol}{208.34 g} \times \frac{1000 ml}{l}}{100 \; ml} = .0447 M \; X ml$$

$$X ml = \boxed{3.80 \; ml \; TEOS}$$

→ Amount EtOH

$$(100 ml - 3.80 - 7.14 - 15.10) = \boxed{73.96 \; ml \; EtOH}$$

Silanol at Particle Surface

Figure 2

ETHANOL - WATER AZEOTROPE
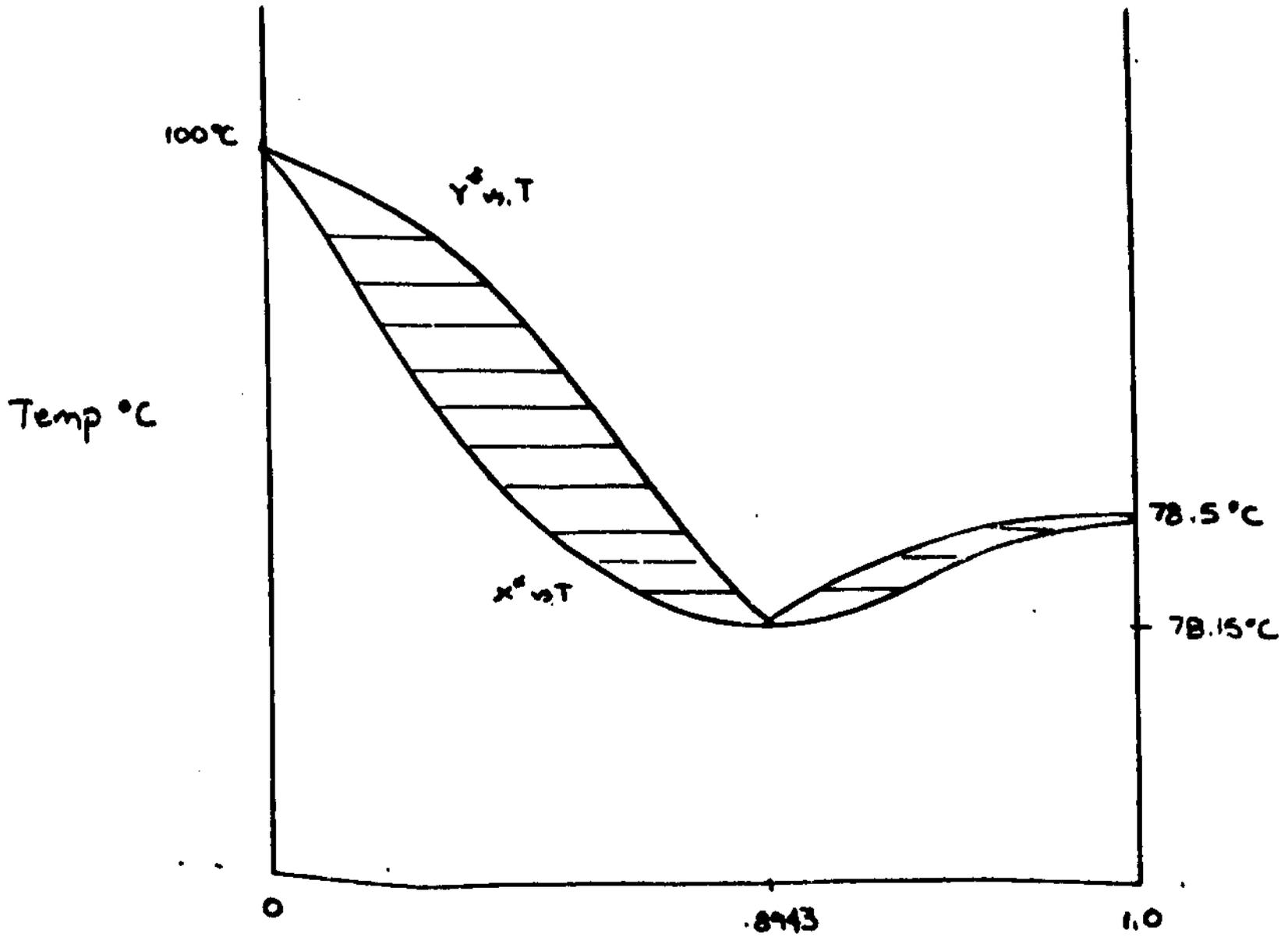
x, y^* - Mole fraction ethanol

$$.8943 = \frac{mol\ EtOH + X_{mol}\ EtOH}{mol\ EtOH + mol\ H_2O + X_{mol}\ EtOH}$$

X_{mol} EtOH = Amount of EtOH needed
to add to reach azeotropic
boiling point composition

Figure 2
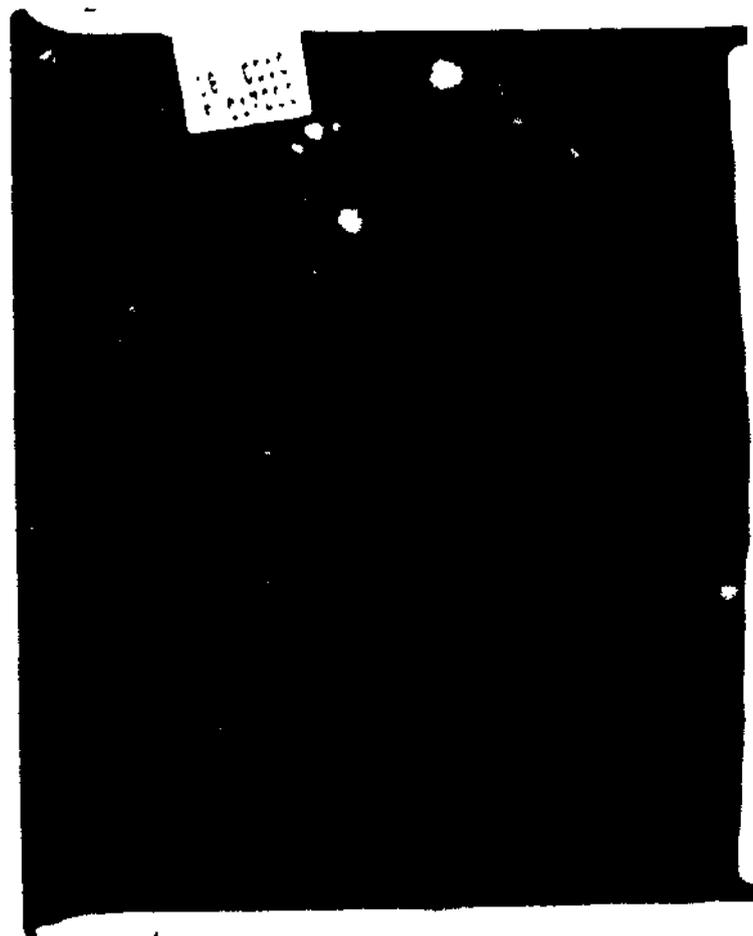
ALCOSOL MICROGRAPH (17,000 X)

Figure 4
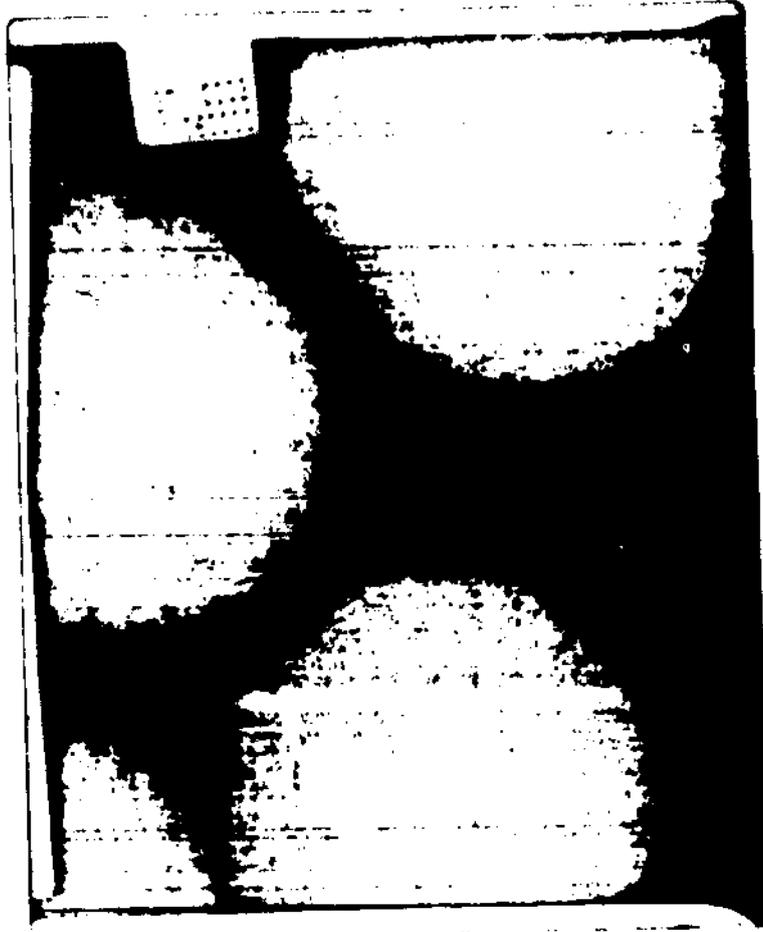
ALCOSOL MICROGRAPH (60,000 X)

Figure 5
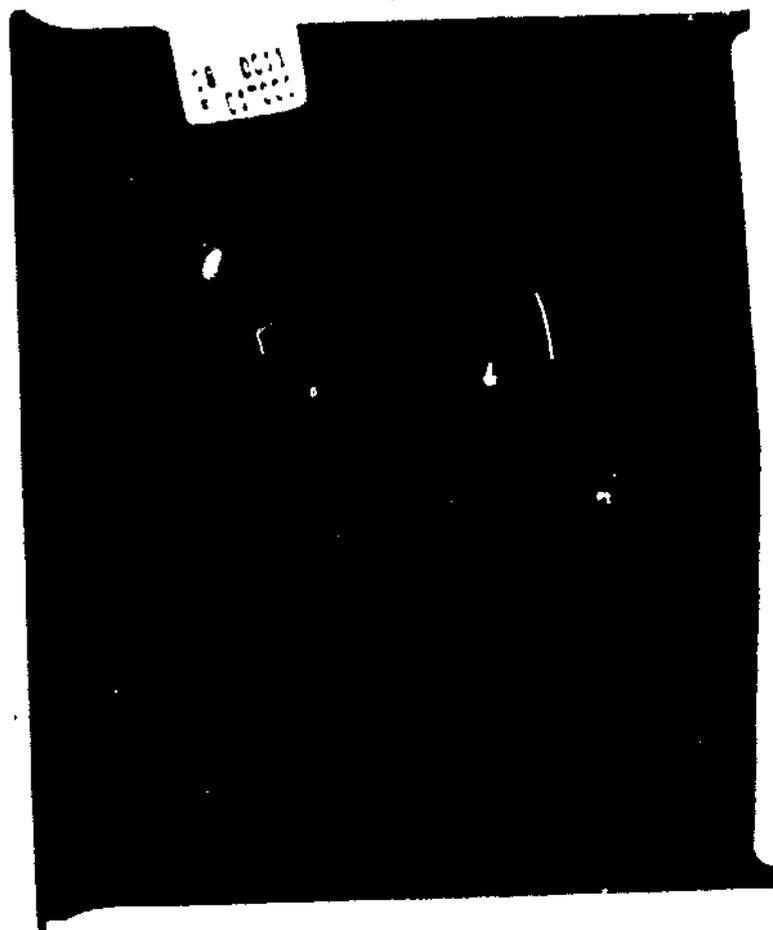
ILLUSTRATION OF CONCENTRATION
EFFECTS

Figure 6
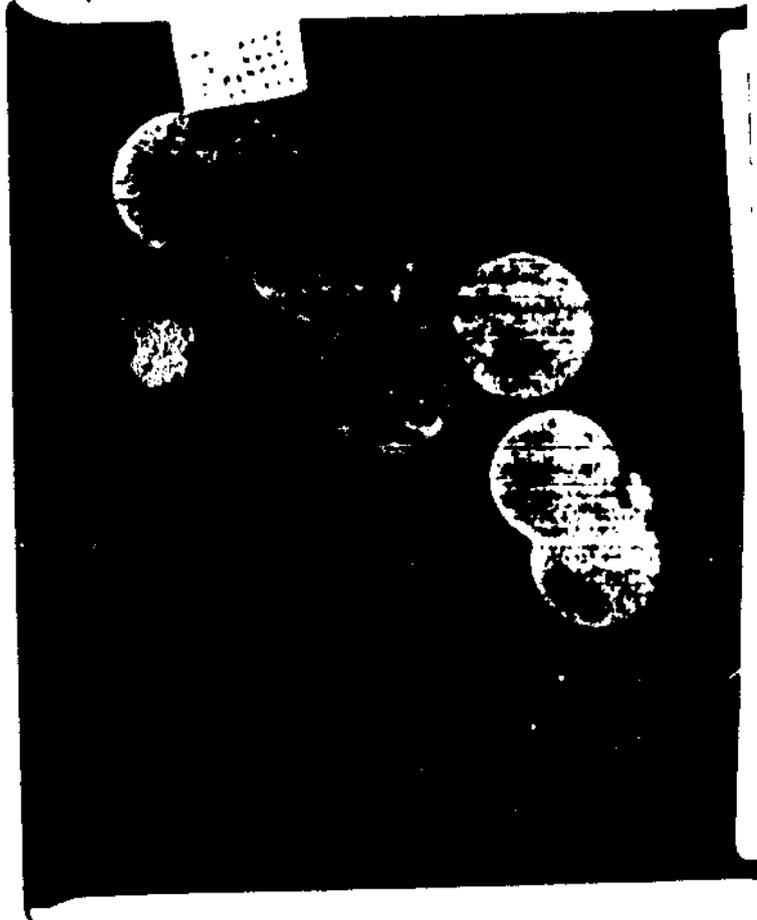
POLY DISPERSITY

Figure 7
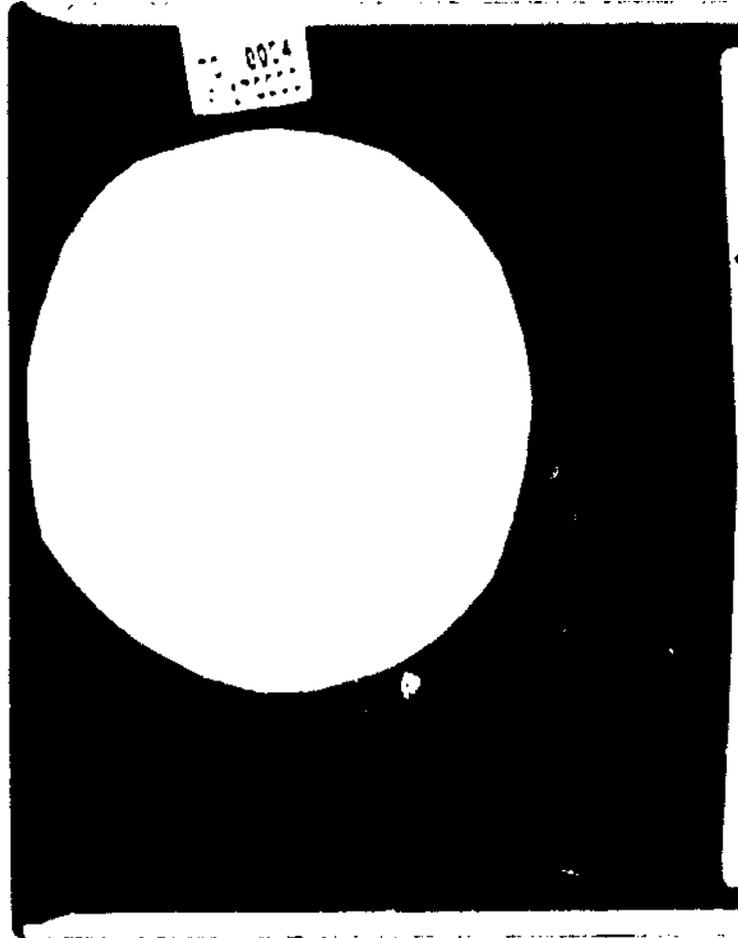
ALCOSOL MICROGRAPH (170,000 X)

Figure 8
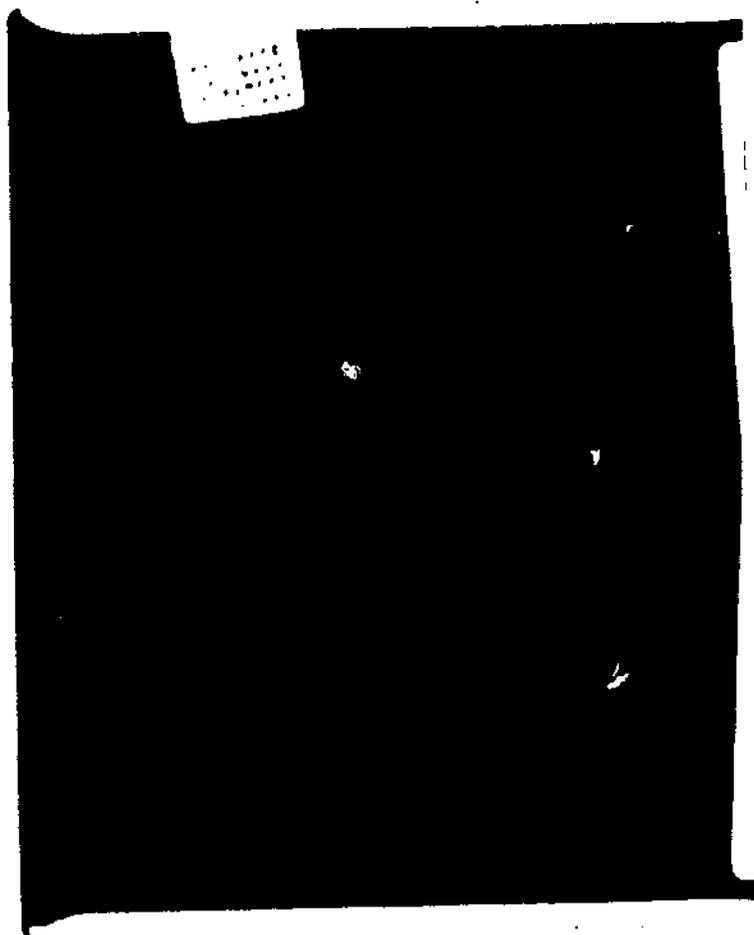
UNSEEDED ALCOSOL

Figure 9

SEEDED GROWTH
ALCOSOL

Figure 10

Figure 11

ELEMENTAL ANALYSIS
UNMODIFIED
SILICA

SCS — Microanalytical Record Card   **FEB 19 1987**

Name ...RICK SUGIHARA... Rcom/Bldg. ...EAG./RAL.. Date ...2/18/87...
Sample No. ...Z... Hygroscopic .... Explosive .... Toxic ....
Elements Present (Formula)......S,O_2......... Analyze For ...C,H, Si ,O...............
B.P./M.P......................... Solvent(s) Used .... Sensitive To................. ....

Theory		Found	Structure, Reaction, And Remarks
TRACE	%C	0.15	Cleaned
TRACE	%H	0.67	rigorously
	%N		Unesterified
43	%Si	43.32	
57	%O		
	%		
	%		

Account # 152095 sub 91   Senior Staff Member ....

                                                     SM—5-86—64239

Figure 12

ESTERIFIED PARTICLE   (17,600X)
MICROGRAPH
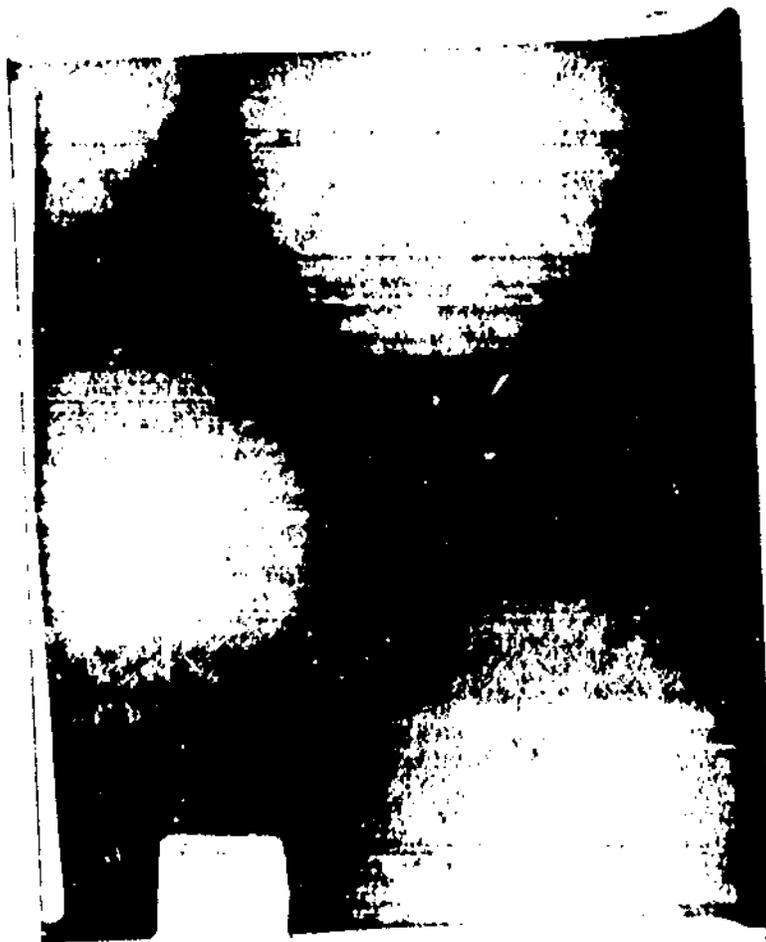
Figure 13

ESTERIFIED PARTICLE (60,000x)

Figure 14

Peak Absent

% TRANSMITTANCE

Figure 15

4000   3800   3600   3400   3200   3000   2800

ELEMENTAL ANALYSIS
MODIFIED
SILICA

30.

SCS — Microanalytical Record Card FEB 19 1987

Name..RICK SUGIHARA...... Room/Bldg...292/KAL... Date..2/10/87...
Sample No........1.......... Hygroscopic...(SiO2)...... Explosive...-———.... Toxic.———...
Elements Present (Formula)...SiO2...C16H37OH/Analyze For...C,H,O,Si.......
B.P./M.P........................ Solvent(s) Used................................. Sensitive To........................:

Theory		Found	Structure, Reaction, And Remarks
3	%C	3.85	
6	%H	1.15	Esterified
	%N		
37	%S	41.86	
54	%O		
	%		
	%		

Account # 1-5-20956 5.659   Senior Staff Member......................
SM.—3-86—64239

Figure 16

APPENDIX B

ELEMENTAL ANALYSIS CALCULATIONS

(In 100g sample)

3.85g Carbon , 1.15g Hydrogen

- Associated hydrogen to stearyl chain

$$3.85g \times \frac{37 \text{ hydrogen}}{18 \text{ carbons}} \times \frac{1g \text{ hydrogen}}{12g \text{ carbon}} = .6595g \text{ H} \Rightarrow .0066 \%$$

- Hydrogen due to silanol + trapped water

$$1.15g - .6595g = .4905g \text{ H} \qquad \Rightarrow .0049 \%$$

TGA
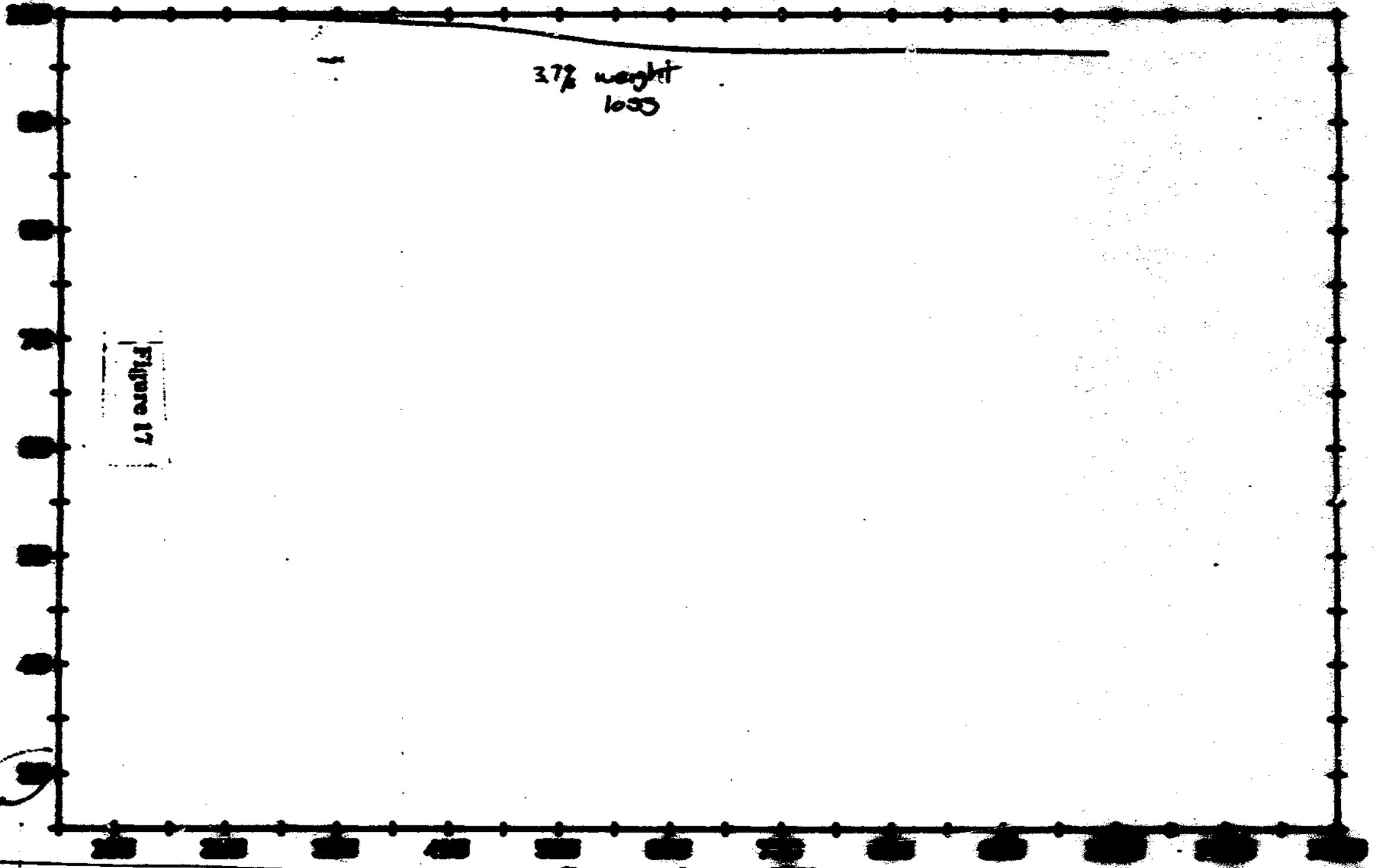
3% weight loss

Figure 17

TGA
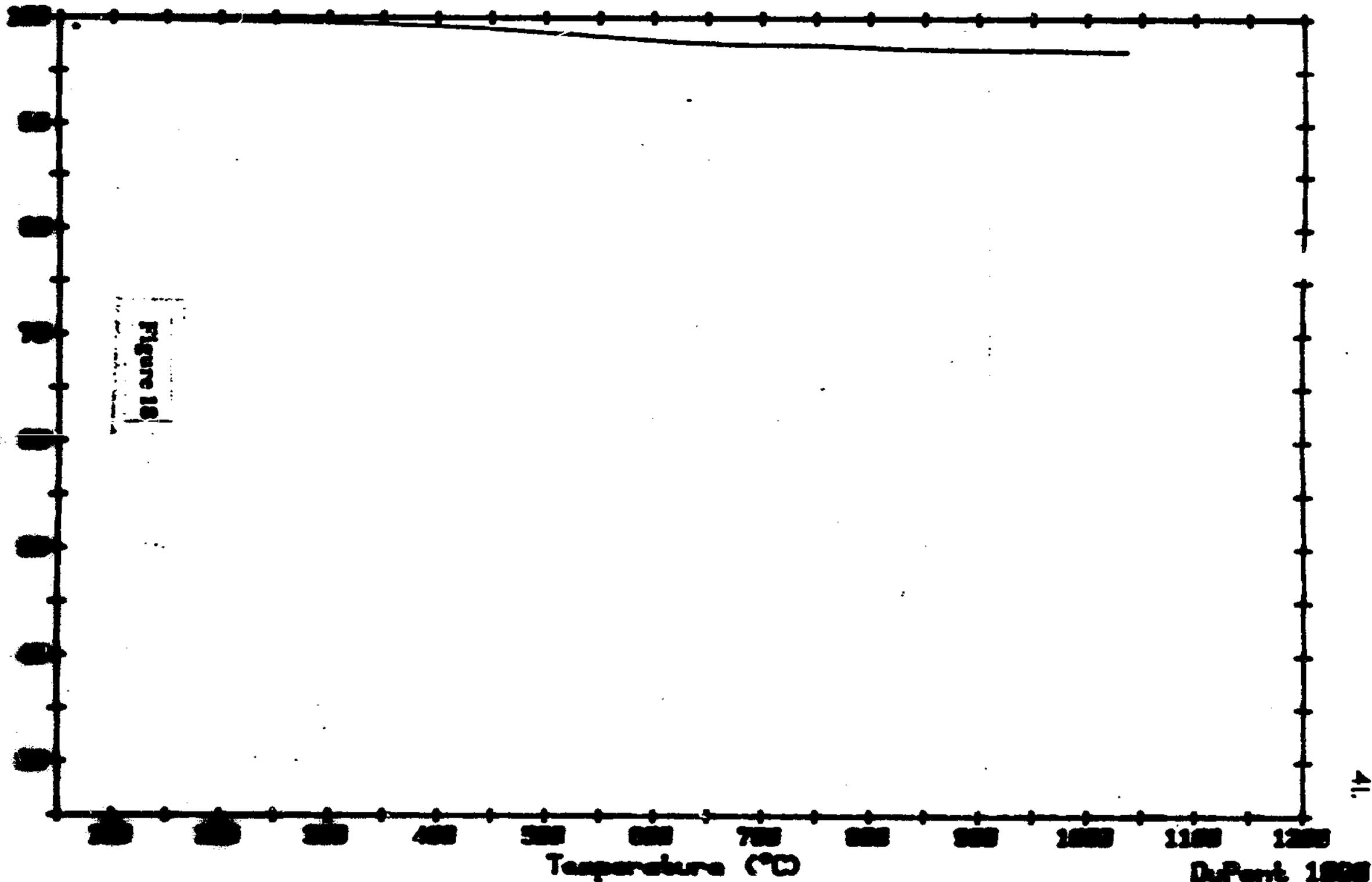
Figure 18

TGA

Date: 5-Apr-87   Time: 23:55:40

Operator: SUGIHARA

Temperature (°C)

DuPont 1090
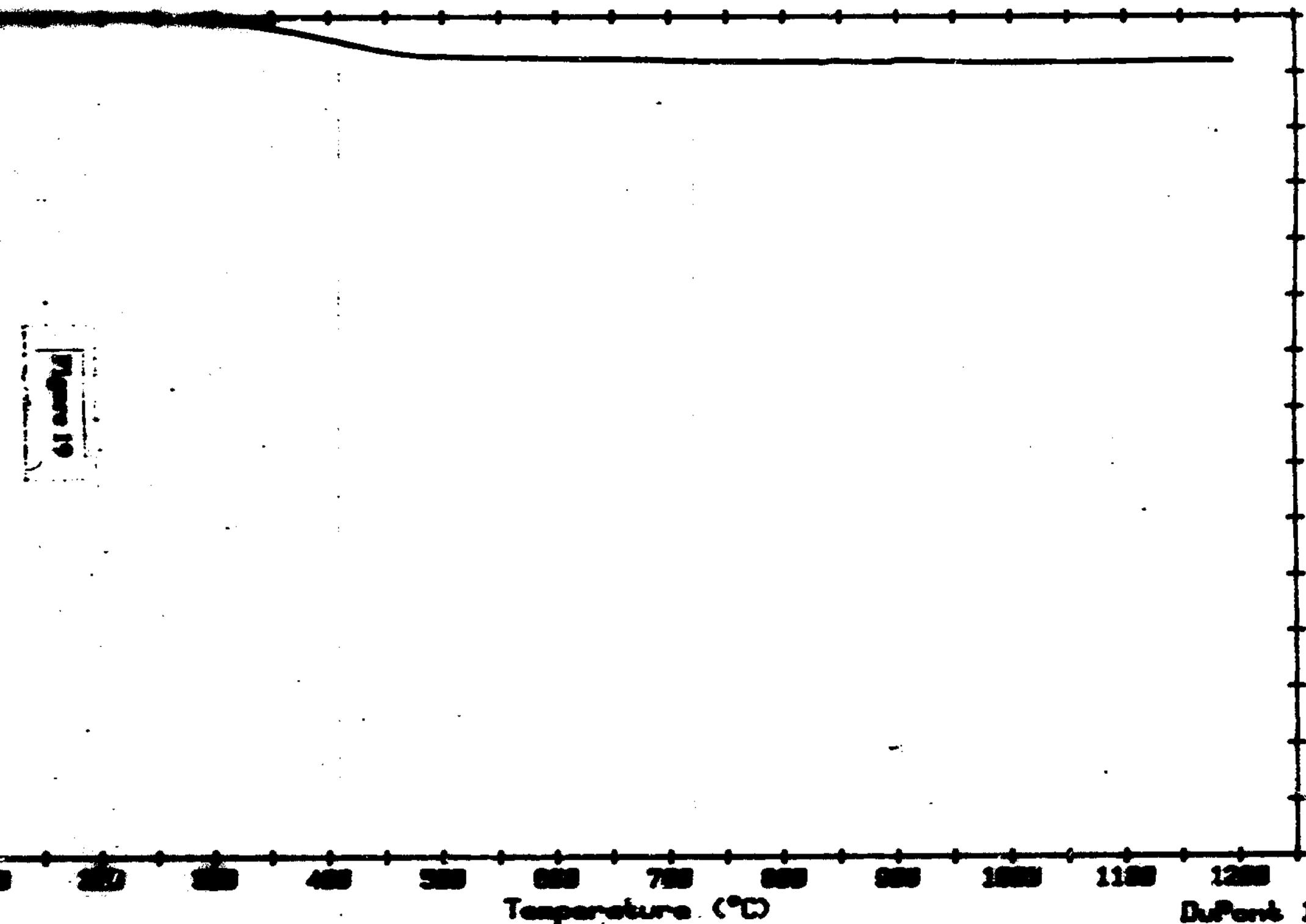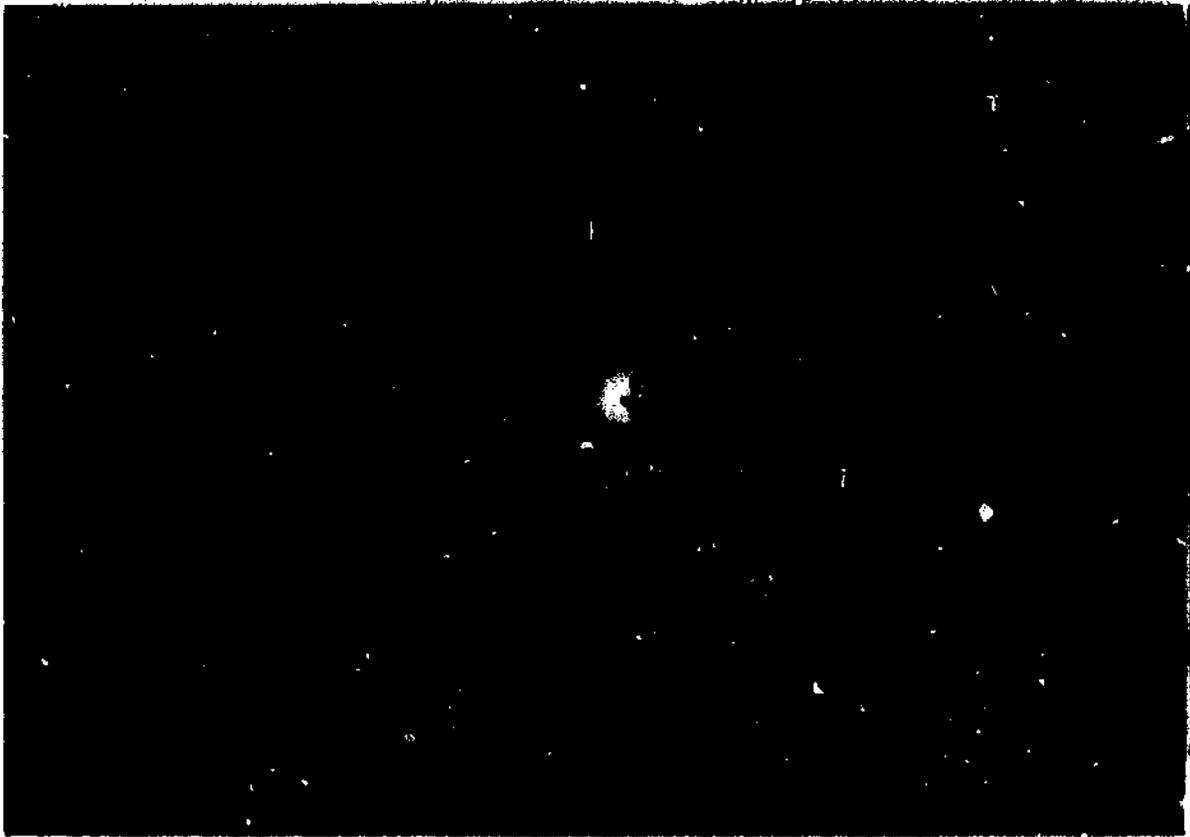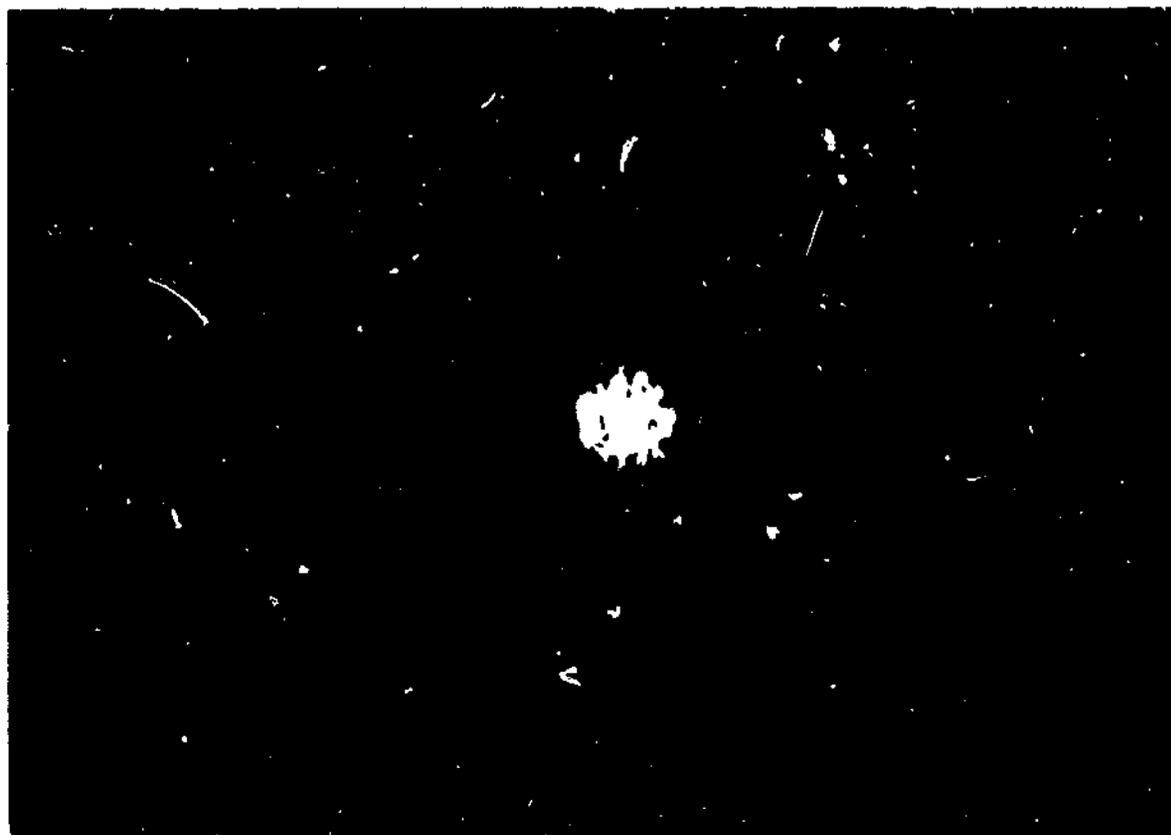
UNCOATED

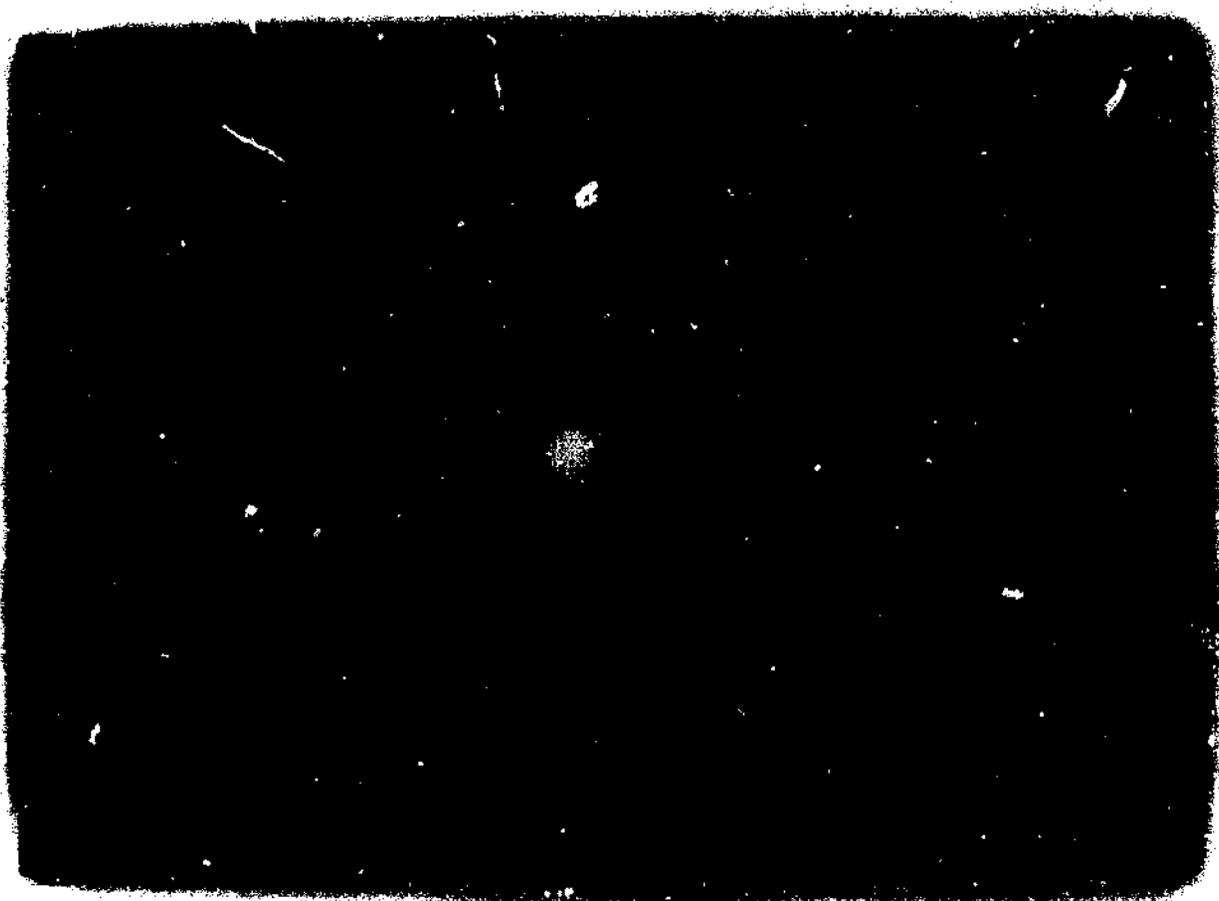COATED

Figure 20
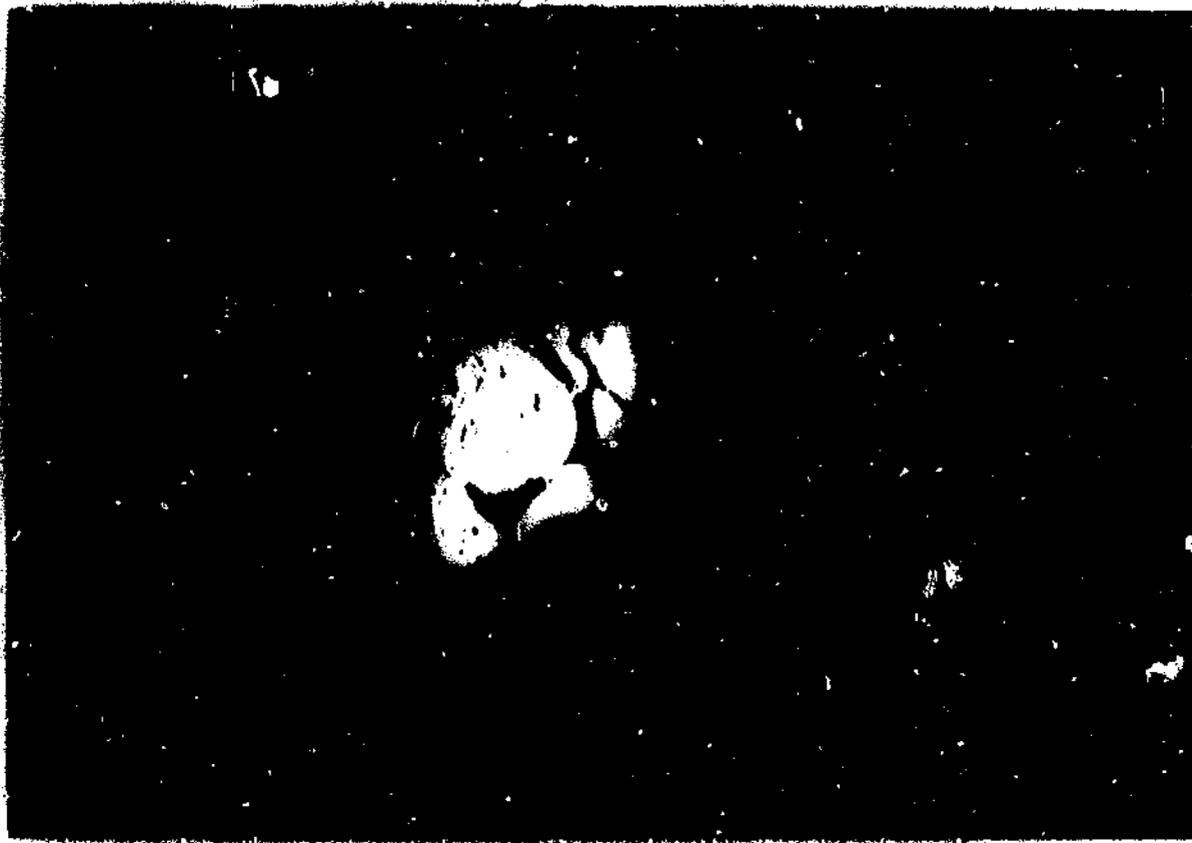
UNCOATED
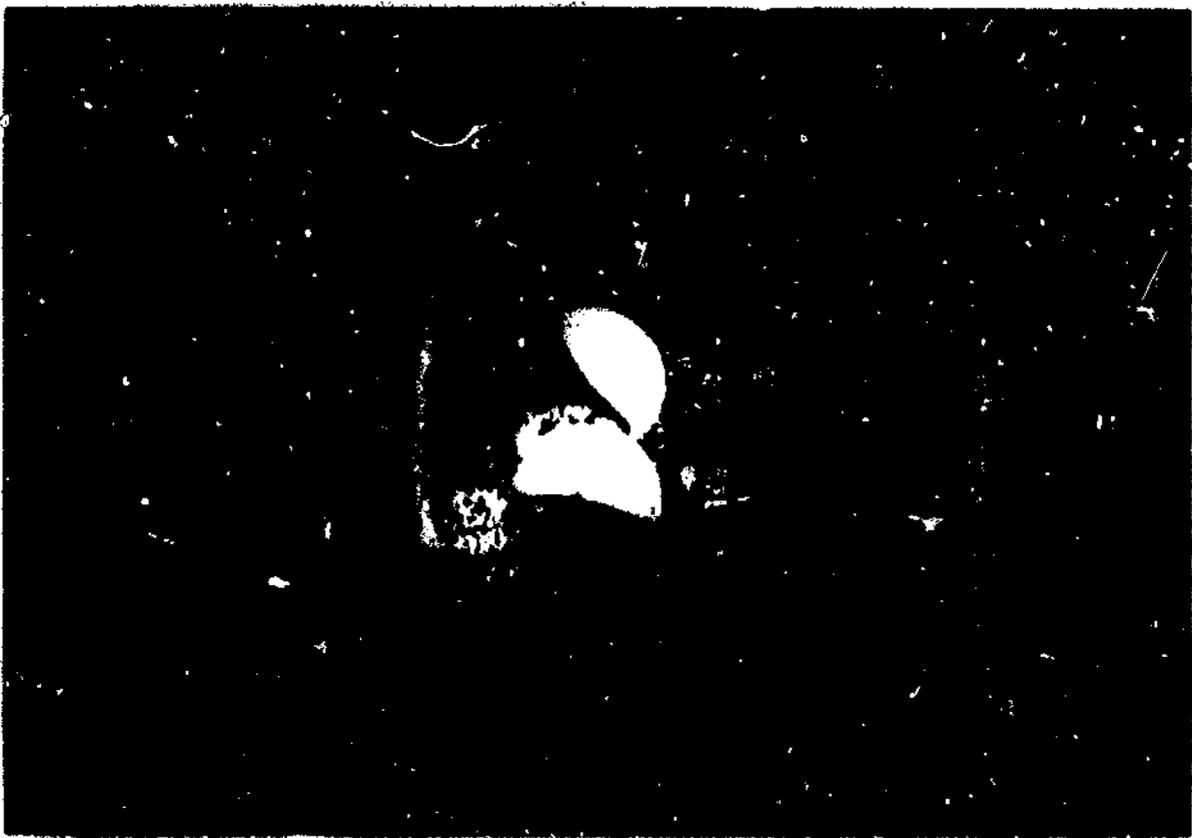
COATED

Figure 21
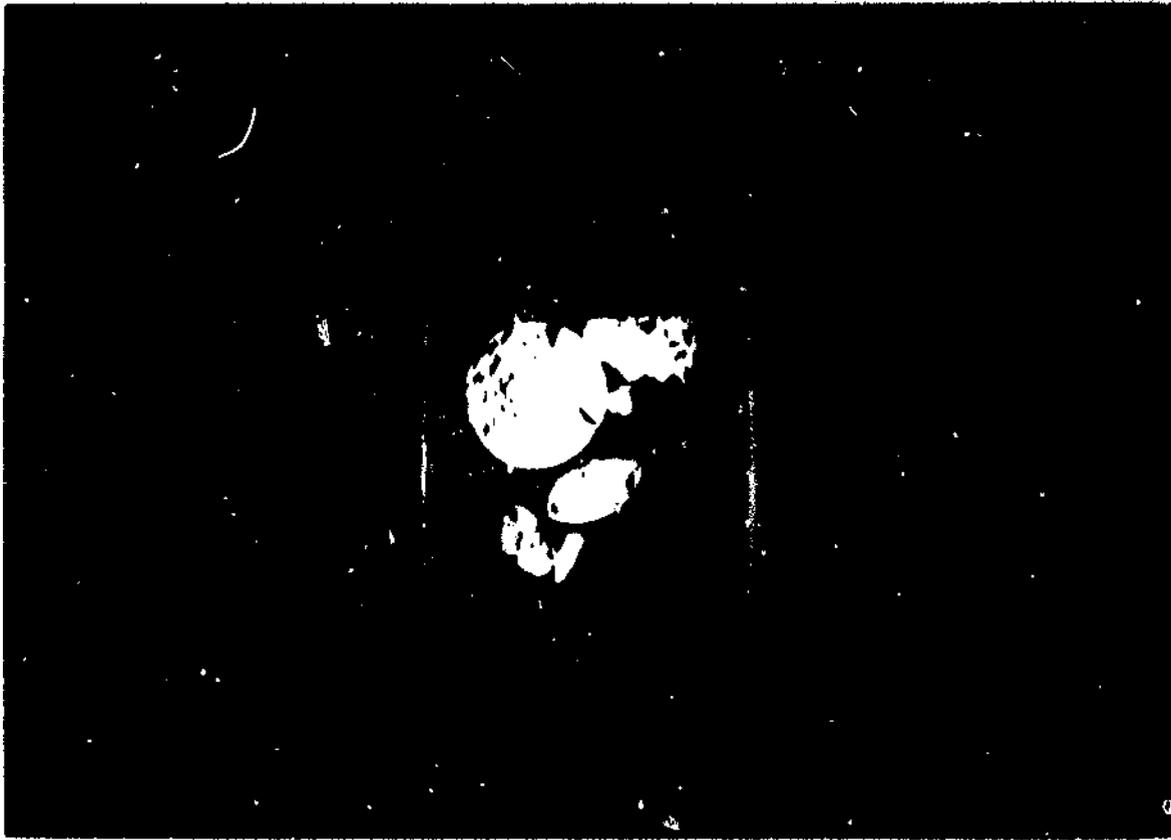
UNCOATED
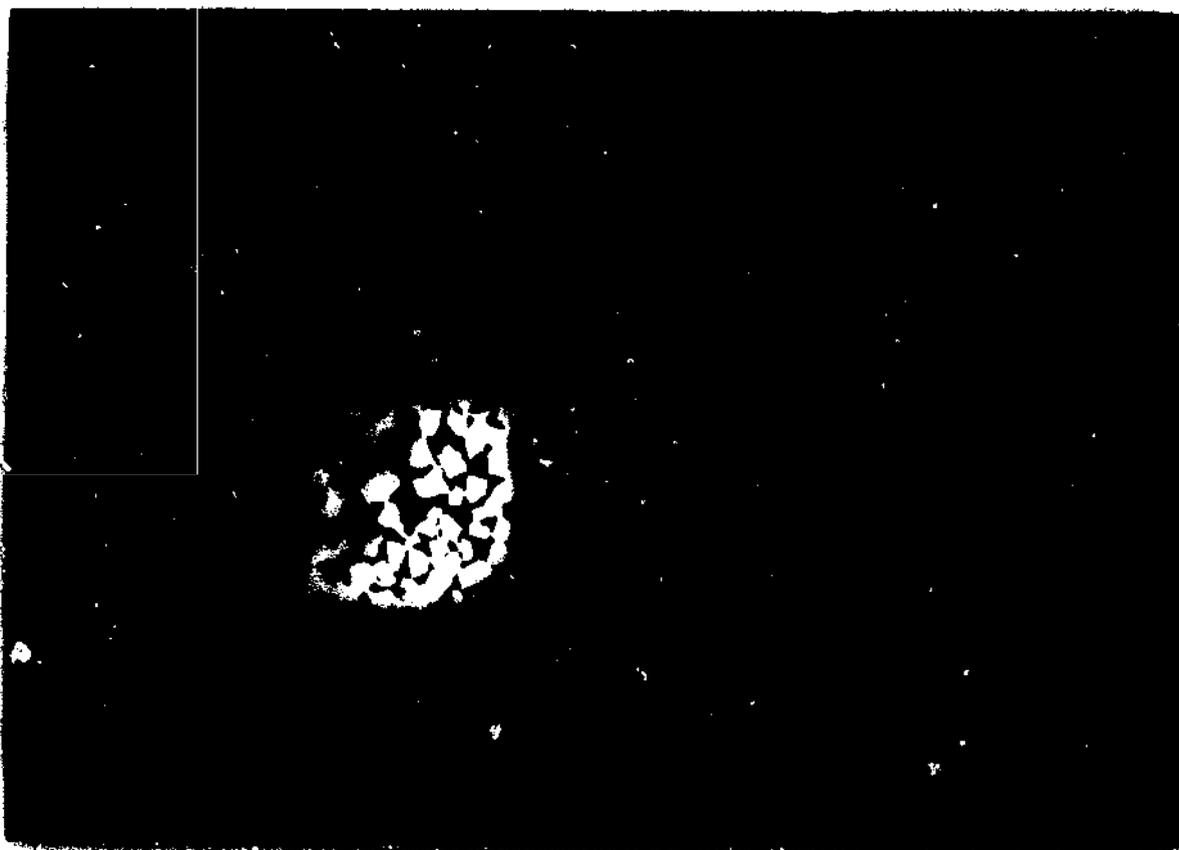
COATED

Figure 22

UNCOATED

Figure 23

SINTERED COMPACTS (1200°C)
ISOTHERMAL

UNCOATED

COATED

Figure 24

HEAT SCHEDULES

4hrs

1000°C

10°C/min   10°C/min

25°C

For compacts in Fig. 22

4hrs

1200°C

5°C/min   5°C/min

25°C

For compacts in Fig. 23

4hr

1200°C

5°/min   5°/min

1hr

25°C

For compacts in Fig. 24