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MRC PROJECT NO. 4530

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**STUDIES OF SURFACE CHEMISTRY OF SOLIDS
IN DISSEMINATION**

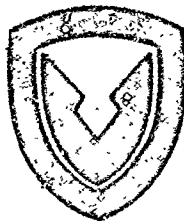
REPORT NUMBER 1

First Quarterly Progress Report

August 1967 - October 1967

by

W. H. Hedley
W. R. Fairheller
G. A. Richardson
D. L. Zanders



**DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Research Laboratories
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010**

**MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO 45407**

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Contract DAAA-15-68-C-0006

MONSANTO RESEARCH CORPORATION
Dayton Laboratory
Dayton, Ohio 45407

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FOREWORD

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ACKNOWLEDGMENTS

This program is being monitored by the Edgewood Arsenal Physical Research Laboratory, Research Laboratories, Edgewood Arsenal, Maryland, with Mr. James D. Wilcox serving as Contract Project Officer.

Others contributing efforts on this contract at Monsanto Research Corporation include Mr. James Baker, Mr. Fred Lowe, and Mr. John Miller.

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DIGEST

The objectives of this program are (1) to develop quality control tests for CS-2 which will insure that the product that is accepted will be reaerosolizable and (2) to study the surface chemistry of powders to determine which factors limit their dissemination by pneumatic and explosive means. Quality control type tests are being developed on CS powders for (1) reaerosolizability, (2) particle size distribution, (3) density, (4) flowability, (5) hydrophobicity, and (6) sintering. Reproducible data on apparent density, bulk density, and fluid density have been collected for CS powders. Statistical analysis of previously existing data on density, particle size, funnel flow rate, elutriation, and dissemination efficiency for both wet and dry samples do not show a strong correlation, except for the case of bulk density and funnel flow rate. This analysis is continuing as new data are becoming available from this program.

Preparation of surface coatings to apply to powders to determine their effect upon dissemination efficiency and the mechanisms which limit it has been started. A pneumatic aerosol dissemination chamber is being installed to provide a facility for testing these coated powders.

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1. INTRODUCTION

This contract involves two related but individual studies: 1) investigation of the surface chemistry of coated solids and the effects of these coatings on disseminability by explosive and pneumatic means and 2) development of quality control tests which characterize CS-2. Although information from each of these studies may influence the other, the two objectives are distinct and separate.

The investigation of the surface chemistry of powders in Task I relative to their pneumatic and explosive dissemination is needed because previous research has yielded results which are as yet unexplainable. Highly flowable powders, such as CS-2 which are more readily disseminable pneumatically than other types of CS show little improvement over the other types when disseminated explosively. Also if CS-2 disseminates pneumatically better than other types of CS, one wonders if there are other types of coatings which would allow treated powders to be disseminated still more effectively than CS-2. The objectives of Task I are to apply different types of coatings to powders, characterize them, and study their performance in dissemination tests in order to gain insight into the mechanisms which limit dissemination of powders.

The goal of Task II of this proposed effort is the development of simple, but significant quality control tests to aid in the selection of the best large scale coating process for CS-2. These tests can later be employed to monitor the quality of the product and will be the basis for preparation of specifications on the mass-produced material. When producing materials on a large scale, controlling all processing variables as closely as is possible in small scale laboratory preparations is difficult. Changes in the process that may affect the quality of the product result. Quality control tests must be developed to differentiate between surface-treated CS-2 that will perform effectively and that which will not be so effective. Until the variables affecting the performance of CS-2 are identified and simple tests are devised to measure these variables, the specific process to be used in producing CS-2 on a large scale cannot be selected.

2. TASK I - NEW COATINGS - FORMULATION, APPLICATION, AND EVALUATION

A comprehensive literature survey on powders was conducted as a first step in this contractual effort. The literature studies could be conveniently divided into three main categories. They were: (1) powder treatment, (2) methods of coating powders, and (3) methods of characterizing the coatings. A summary of the literature survey is included in the next section (2.1).

2.1 Literature Survey on Powders

2.1.1 Powder Treatments

Compounds used to treat powders are selected for their ability to improve flow (such as alkyl aryl sulfonates), to reduce caking (such as fatty acids or amines), to reduce electrostatic effects (such as quaternary ammonium salts), or to control hydrophobicity (such as perfluorinated compounds). Many compounds that contain silicon also improve flow. Flow-improving compounds are usually applied in quantities from 0.1-5% by weight. Some powders require only one coating to achieve the desired qualities while other powders require one compound to increase lubricity and another to control hydrophobicity and electrostatic charge. In selecting coatings for powders one must check to be sure that ones which benefit one specific property do not adversely affect others. A list of compounds and their use are given in Table 1.

2.1.2 Methods of Powder Coating

The commercially available blenders are usually one of four types (Ref. 40); the tumbler, the rotating shell, the Mueller mixer, and the fluid energy mill. The tumbler, or rotating shell blender has a disadvantage common to all of the blenders except the fluid energy mixer - powders in the subsieve range tend to form loosely agglomerated particles or pellets in this equipment. Those blenders with a stationary shell have several added disadvantages for use with powder. Because of the increased shear forces, static charge buildup becomes a problem. In the Mueller mixer densification of the final mix and frictional anchorage of particles to one another are the predominant disadvantages.

The jet mill or fluid energy mill has many advantages: minimum contamination, no attritional heat due to the Joule Thomson effect, lower static charge effects, maintenance is minimized by lack of moving parts, and minimal demixing (Ref. 41).

Table 1

COMPOUNDS AND THEIR USE

A. <u>Flow Improving Compounds</u>	<u>Use</u>
1. Starch, 0.5% siliconized talc, mg stearate, Al, stearate, poly-(ethyleneglycol) (Ref. 1)	Drugs
2. SiO ₂	
3. Colloid (gelatin, gum arabia) or polyvinyl alcohol plus silica and talc (Ref. 3)	Pharmaceutical powders
4. Amylopectin, cellulose, poly-(vinylpyrrolidone) gelatin, alginic acid, polysaccharides, natural gums, and resins 0.8-5% wt of coating dissolved in H ₂ O alcs., ethers, ketones, or halohydrocarbons (Ref. 4)	Powders
5. 0.5-15% wt of o- and p-vinylphenylmethane sulfonic acid or salt (Ref. 5)	Free flowing ammonium bromide
6. Powdered NH ₄ NO ₃ containing mono or dioctadecylhydrazine, stearoyl hydrazine, octadecylguanidine or octadecylcarbamyl guanidine 0.05-0.1% (Ref. 6)	Improves flow
7. Polyphosphates (NaPO ₃) _x , diphosphates, Na ₄ P ₂ O ₇ , ethylene glycol, poly(vinyl alc.), Et ₂ NH, Et ₃ N, and piperazine (Ref. 7)	Dispensing agents
8. Aliphatic polyhydroxyl, polyethylene glycol - its esters or ethers (Ref. 8)	Free flowing starch
9. Hexamethylenetetramine (Ref. 9)	Free flowing urea and good storage

Table 1 (Continued)

	<u>Use</u>
10. Sulfonated esters of hydrogenated fatty acid esters with sulfonated fatty acid with optional $\text{Na}_4\text{P}_2\text{O}_7$, liquid sodium silicate, Na_2SO_4 , fatty acid ethanoline (Ref. 10)	For pourable detergents
11. Salts of esters of fatty sulfonic acids (15-50%) (Ref. 11)	Pourable washing agents
12. P-vinylphenylmethane sulfonic acid (or salt) (Ref. 5)	Free flowing ammonium bromide
13. Thin layer of oil, metallic oxides, carbonates, phosphates calcium silicate (Ref. 12)	Improves flow when humidity causes antilump
 <u>B. Anticaking Agents</u>	
1. Nitrates, hydrochlorides and acetates of amines of saturated or unsaturated hydrocarbons of $\text{C}_8\text{-C}_{24}$ added in amounts of 0.04-0.05% by wt (Ref. 13)	Lumping inhibitor in NaNO_3 and KNO_3
2. Fatty acids such as palmitic, stearic, or naphthenic acids (Ref. 14)	Anticaking agent for granulated fertilizers
3. Ferrous hexacyanomanganate (Ref. 15)	Noncaking NaCl
4. Ferric ammonium citrate, ferric ammonium tartrate, ferric ammonium gluconate (Ref. 16)	Noncaking NaCl
5. 2% charge dope with 2.5-10% surface active agent and/or water repellent material. Charge = talc, chalk, sand, clay, kaolin. Doping additive = $\text{RNH}_2\text{-R}$ ($\text{R} = \text{C}_8\text{-C}_{22}$) salt of RNH_2 with HCl, HOAc or alkyl-carbanic acid (Ref. 17)	Antilumping agent in pulverized and granulated products

Table 1 (Continued)

	Use
6. Fatty acid mixture with fatty amines (Ref. 18)	Anticaking of salts and fertilizers
7. Finely divided Na alumino silicates reacted with acid in controlled conditions (Ref. 19)	Anticaking agent for hydroscopic salts
8. $K_2[TiO(C_2O_4)] H_2O$ (Ref. 20)	Anticaking agent for NaCl
9. Fatty acid or salt, silicone aliphatic amine or a combination (Ref. 21)	Anticaking agent for NaCl
10. Ferrocyanide, ferricyanide, nitrocyanide, carbonyl ferrocyanide, or nitrotriacetamide, treated with 0.1-5.0% liquid organic siloxanes (cyclic) such as $(MeHSiO)_4$, $(MeHSiO)_5$, etc., mixed 5-500 ppm (Ref. 22)	Anticaking agent for NaCl
11. Treated vermiculite (Ref. 23)	Noncaking agent for fertilizers
12. Finely divided dried linseed flour, rice flour, or alfalfa flour (Ref. 24)	Prevents caking in livestock feed
13. Octadecylamine 0.5-1%, $K_4[Fe(CN)_6]$ 0.01%, $K_4[Fe(CN)_6]$, $PbCl_2$, MgO , dolomite (Ref. 25)	Anticaking agent for NaCl
14. Alkaline earth silicate particles in aq. medium (Ref. 26)	Anticaking NaCl
15. 2% nonylphenyl pentadecylene glycol ether with 35% metasilicate pentahydrate + 52.2% sodium tripolyphosphate + 10.5% sodium primary phosphate monohydrate (Ref. 27)	Noncaking alkaline detergent
16. Salts of the amphoteric oxide on hydroxide (Fe^{III} , Cr^{III} , Al, Zr, Cu^{II} , a mild alkali (NH_3 , $CaCO_3$, etc.) and optional salt taking up H_2O of crystallization (Ref. 28)	Anticaking agent for granulated ammonium sulfate nitrate

Table 1 (Continued)

	Use
17. Liquid activated di- or tri-olefin polymer (mol wt 500-40,000) hardened on surface 0.1-0.6% (Ref. 29)	Noncaking agent for fertilizer
18. Kaolin clay coated with NaC_{8-12} alkylaryl sulfonate by dry blending and pulverizing 0.5-2.0% (Ref. 30)	Anticaking agent for hygroscopic fertilizers
19. Silicon dioxide 2% (Ref. 31)	Anticaking agent for food
20. Attapulgite clay, $\text{Na}_4\text{P}_2\text{O}_7$ (Ref. 32)	Anticaking agent for fertilizer
21. Propylene oxide condensed with fatty amine containing 14-20C (Ref. 33)	Anticaking agent
22. Thin layer $\text{Al}(\text{OH})_3$ suspension containing an organic oxy acid (citric, tartaric, etc.) $\text{Al}(\text{OH})_3$ conc. 0.0009-0.0018% oxy acid conc. 0.0008-0.0026% (Ref. 34)	Anticaking agent for NaCl
23. Synthetic silicas (ppt and pyrogenic), clay, synthetic carbonates (ppt), aluminas (ppt and pyrogenic), carbon black metallic powders (Ref. 35)	Anticaking agents
24. Hexamethyldisilizane .25-1.0%	Improves flow of CS-2
25. Chlorosilanes	Used to increase the effect of milling
26. Hydroxypropyl Me Cellulose (Ref. 36)	Noncaking, edible coating for organic acids

Table 1 (Continued)

	<u>Use</u>
<u>C. Antistatic Coatings</u>	
1. Quaternary ammonium salts of poly-(epichlorohydrin) (Ref. 37)	Antistatic agent disperser and emulsifier
2. Hexamethyldisilazane	Static charge reducer
3. Metal salts of imidazoline-type amphoteric, surface active agents (Ref. 38)	Internal antistatic agents for molded polypropylene
<u>D. Hydrophobic Coatings (Ref. 39)</u>	
1. Tetrakis (3,3,3-trifluoropropyl) silane	
2. Tetrakis (2,2,2-trifluoroethyl) silane	
3. Perfluorosilicas	
4. Fluorinated β -diketones	
Ex: 1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione	
5. SiOH and Hexamethyldisilazane	

Another advantage of fluid energy mills in the coating of powders is that a classifier may be used simultaneously to give a minimum particle size distribution.

Its main disadvantage for agent grinding is that it is difficult with this method to completely confine the materials while grinding.

Table 2 lists the commonly used blenders and their use.

2.1.3 Coating Characterization

2.1.3.1 Storage

The storage stability of a treated powder may be evaluated by compression tests (Ref. 42) in which small plastic sachets of the powder are stacked and a known weight applied. After the desired length of time the sachets are opened and contents shaken on a coarse sieve. The portion passing through the sieve is weighed and the difference between this and the original weight gives the percentage caking. The stored powder may also be subjected to any one of the following tests.

2.1.3.2 Aerosolization

Aerosolization qualities of a powder are commonly determined by measuring the sedimentation rate and particle size distribution of a dispersed powder in a cubic meter chamber. Knutson, et al. (Ref. 43), have determined the coagulation rate of ten-micron aerosols of cornstarch and spray-dried saccharin by pneumatically disseminating the powder in a cubic meter chamber with turbulent mixing and then counting the number of agglomerates with a microscope.

2.1.3.3 Flow

Flow is usually determined by measuring the angle to the horizontal assumed by a conelike pile of material (Ref. 44). This is defined as the angle of repose and there are many variations of this. The three-dimensional angle of repose is obtained by allowing a fixed weight to fall from a fixed height, forming a conical heap of height h and radius r . The tangent of the angle of repose = h/r (Ref. 45).

The internal kinetic angle of repose (Ref. 44) is the angle between the horizontal and the plane which visibly separates those particles which are sliding down the surface of the powder and those which are rotating with it in a hollow drum. The angle

Table 2

COMMERCIAL BLENDERS

Commercial Blenders (Ref. 41, 46)	Use
1. Tumbler	Gentle blending.
2. Stationary Shell	Low density, finely divided materials that aerate rapidly to fibrous or sticky materials.
A. Ribbon Mixer	
B. Vertical Screw Mixer	Primarily for free flowing dry solids.
C. Muller Mixer	Useful for mixing requiring certain types of aggregate breakdown, frictional anchorage of particles to one another and densification of the final mix. Fluid or stick materials should be avoided.
D. Twin Rotor	Useful for non free flowing solids.
E. Single Rotor	Intense dispersion and disintegration.
F. Turbine Mixer	Suitable for free flowing dry materials. Adaptable to liquid-solid mixing and application of coatings.
3. Shell and Internal Device Rotate	Mixing of free flowing solids not requiring the shearing and compression of the Muller
4. Impact Mixing (Ref. 47)	High speed rotor
A. Mikro-Atomizer	
B. Raymond Vertical Rotor	
C. Micronizer	Fluid energy type
D. Reductionizer	
E. Eagle Mill	

of friction (Ref. 44) is the angle to which a particular base must be elevated before the powder begins to slide upon it. The angle of fall is the angle resulting when a 111 g steel bushing is dropped on a plate with a powder heap five times from seven inches. The angle of difference is the difference between the angle of repose and the angle of fall.

2.1.3.4 Hydration

The critical relative humidity of a material has been ascertained by Burak (Ref. 42) by exposing equal weights of the host powder in Petri dishes placed in a series of desiccators maintained at known relative humidities for 48 hrs. The amount of hydration or dehydration at a particular relative humidity could then be determined by weight gain or loss, respectively.

2.1.3.5 Particle Size Analysis (Ref. 48)

There are three types of analyses commonly used for particle size determination: optical, gravitational, and inertial.

Enlarged images may be made from either electron or light microscope. The images can then be scanned by an optical scanner. Flying spot scanning (Ref. 49) is another method of optical size determination. An intense light spot slowly scans a cathode ray tube and is optically imaged down through a conventional microscope. The imaged light scans a fixed microscope field and the variation in spot intensity is amplified from a photomultiplier tube. Particle sizing is determined from pulse width selection.

Many types of sedimentation methods (Ref. 50, 51) are currently used for particle size analysis. These techniques depend upon Stokes' law and in order to solve the equation you need to know only the time required for a particle to move a given distance. This procedure becomes very tedious when applied to large numbers of particles.

Calbeck and Harner (Ref. 51) have used a method in which one pan of a single beam balance is placed in a settling chamber, in which is a particular medium. The powder dispersion is introduced into the liquid. The time required for different amounts of powder to settle out on the pan is then plotted against time. From this the percentage particle size can be determined.

The simplest fluidized system for size analysis is the vertical gravity elutriator (Ref. 52). As the fluidized powder flows upward through a series of elutriation columns, velocity is decreased from one to the next by increased diameter of each succeeding column. The most widely used equipment for elutriation is the centrifugal or inertial separator. It simply directs a gas suspension through an abrupt change in direction. The centrifugal separator carries out the same process, but spins the gas to impart high centrifugal force to the particles. The oversize material is thrown to the periphery while the undersize material is exhausted.

2.1.3.6 Bulk Density (Ref. 53)

Nash (Ref. 54), et al., determine the bulk density of Cab-O-Sil treated carbowax by sifting the sample through a small funnel covered with a wire mesh screen and into a cylindrical container of known dimensions. The container is filled to the brim and excess powder scraped off.

Bulk density should always be specified as to the type of measurements which have been made; fluid bulk density, aerated bulk density, packed bulk density, etc.

2.2 Coating Formulation and Application

In an effort to delineate the chemistry and surface characteristics of disseminable powders, a study of model compounds has been undertaken at MRC. It is planned that the disseminability of powders coated by various methods of application and with different compounds will be studied. Hopefully, these studies will define the coatings and the methods for applying them which lead to optimum disseminability by both pneumatic and explosive means.

The objectives of this effort are to study the mechanisms by which coatings adhere to solid surfaces (whether chemical, electrical, or physical); to determine the nature of the forces involved in these mechanisms (whether electrostatic or hydrogen bonding); and to analyze the surface properties of model compounds in an effort to determine the effect of preparative methods on surface phenomena. The aforementioned model compounds include CS, CS-1, CS-2, Cab-O-Sil, Aerosil, and HMDS-coated Cab-O-Sil.

The mechanism of particle adhesion is highly controversial. It is possibly due to three factors: chemical, electrical, and/or physical bonding. Since 1963 a new theory has appeared which states that all types of adhesion are nothing but adsorption, a mechanism of the solid surface (Ref. 48, 53). In order to gain an understanding of the effects of surface on dissemination, it will be necessary to distinguish which of these mechanisms are actually the most important in limiting both the explosive and pneumatic processes.

It is our intention to study surface phenomenon by coating the models with specific compounds that have been carefully chosen in order to isolate and enhance the effects of the surface forces. Hopefully, the forces responsible for inefficient dissemination will be identified. The compounds proposed for coatings are: (1) a fluorinated β -diketone, such as 1,1,1,2,2,3,3,7,7,7-decafluoroheptane-4,6-dione, which should react with surface-OH groups of the substrate to give a tightly bound, hydrophobic coating; (2) a fluorinated silane, such as tetrakis(3,3,4,4,5,5,5-heptafluoropentyl) silane, a hydrophobic compound which should remain relatively inert to hydrogen bonding and electrostatic forces. This compound could conceivably be ideal for use as a dissemination coating; (3) a fluorester, such as pentaerythritol tetra(trifluoroacetate), which has a strong hydrogen-bonding potential. Therefore, it would serve as a basis for testing the validity of the hydrogen-bonding concept. In addition, it would allow a comparison of the lubricating properties of carbon and silicon (see compound 2); (4) an antistatic agent, such as a quaternary ammonium salt, which would determine the relevance of antistatic coatings. A specific powder which is not influenced by hydrogen bonding must be used in order to separate the two effects; (5) a hydrophobic silicic acid and/or a specific colloidal silica, such as Aerosil, which would impact hydrophobic character to powders, and which demonstrate antistatic action. In addition, the flow characteristics would be improved; (6) an inert filler, such as silicon carbide, which will improve flowability. These materials would be inert to chemical reaction and would be unaffected by hydrogen bonding and electrostatic attraction; (7) a lubricant, such as an organo-silicone, which would give a hydrophobic coating of molecular thickness and tend to minimize electrostatic charging. Concomitantly this coating could act as a lubricant between particles.

The fluoroester, tetrakis(trifluoroacetyl) pentaerythritol (TAP) $[(CF_3COOCH_2)_4C]$, has been prepared and its structure confirmed by NMR data. As expected, the properties of the molecule are somewhat unusual due to the perfluoroacetyl "shield" about the central carbon atoms $[-(CH_2)_4C]$. For example, simple esters, such as TAP, are usually soluble in both polar and non-polar organic solvents. However, TAP has a much greater solubility in highly polar compounds, such as ether, acetone and dioxane, than in non-polar compounds, such as benzene and hexane. This fact tends to confirm the anticipated hydrogen-bonding capabilities of TAP. These capabilities are further demonstrated by the difference in the solubility of TAP in carbon tetrachloride and in chloroform. TAP is very soluble in chloroform, a strong hydrogen-bonding solvent, it is sparingly soluble in carbon tetrachloride, a non hydrogen-bonding solvent. Although it has the typical opaque, waxy appearance of a solid fluorocarbon, TAP is a well-defined crystalline solid.

Infrared spectroscopy studies have been initiated with model compounds (Cab-O-Sil HS-5 and Aerosil) in order to determine the nature of their surfaces. Infrared is the analysis of choice in that it has yielded more information on surface characteristics (in catalysis research) than has FMIR.

2.3 Aerosol Dissemination Chamber for Evaluation of New Coatings

An aerosol dissemination chamber approximately 6 feet in diameter by 11 feet high has been constructed as shown in Figure 1. The chamber is presently installed in the laboratory area and outfitting for the various accessories will begin soon. A fan and fan motor have been purchased and will be installed in the upper portion of the chamber. Other accessory equipment will include dissemination equipment for either nozzle or pneumation dissemination, decon spraying and removal piping, lighting and viewing parts, and a laser and photocell for following the decay of the aerosol. Sampling accessories will also be designed and constructed in the near future for use with the chamber. As this unit will be used in the later parts of the research program, the work is being conducted as time permits without interfering with the major effort of the first six months in the quality control test development.

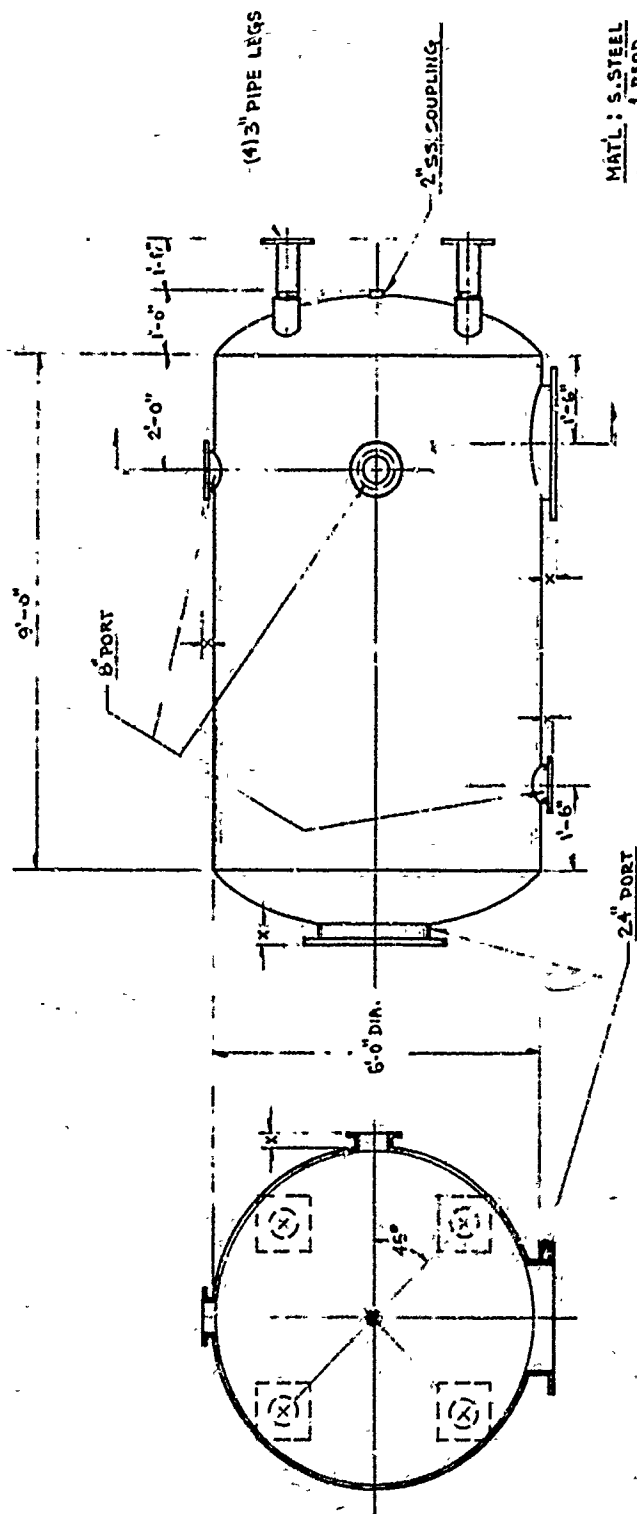


Figure 1. Sketch of Aerosol Dissemination Chamber.

3. TASK II - DEVELOPMENT OF QUALITY CONTROL TESTS

The objectives of this task are to (1) develop quality control tests for reaerosolizable powders and (2) study the relevance of these tests to reaerosolizability of powders. Theoretical considerations suggest that the following tests might be of value: particle size, density, flowability, hydrophobicity, and sintering. Sintering, the agglomeration of particles by mass migration at ambient conditions, is included as a measure of change of particle size with time upon storage. Since reaerosolizability is to be the criterion for good performance in this application, development of tests for this property are also important.

Quality control tests have several special requirements which differentiate them from property tests in general. These requirements are:

- (1) the test should not be expensive to set up
- (2) it should be carefully described in writing so that everyone understands the exact procedure to use and does it in the same way
- (3) the test results must be reproducible
- (4) it can be run by inexperienced people with virtually no special training who obtain the same result as other similar people measure
- (5) the results significantly test an important property of the material being made.
- (6) the tests can be run in a short period of time so that the results can be obtained quickly and the material accepted or rejected without a long delay.

These requirements will be carefully considered during our development program.

The relevance of the tests being developed to reaerosolizability will be determined statistically. The powders we have been furnished will be rated as to their reaerosolizability. Tests for reaerosolizability are being developed. It is hoped that at least some of the other tests being developed will correlate statistically with these reaerosolizability data and thus establish their relevance. Statistical tests for correlation will also be made between all of the other properties being measured in this program.

The following section described the tests being developed to measure (1) reaerosolizability, (2) particle size, (3) density, (4) flowability, (5) hydrophobicity, and (6) sintering. The results of initial statistical correlation attempts are also reported.

3.1 Reaerosolizability

Reaerosolizability is the term which describes the ability of a powder which has been deposited on the ground to be aerosolized again when mechanically disturbed. We have started work on an elutriation device which we hope will measure this property. The design of our candidate elutriation apparatus has been finalized. As in the GCA elutriation (gas filtration) because of the large specific surface and high resistivity of the MF type millipore filter (used in our elutriator) electrostatic charges are generated and held. This negative charge prevents the passage of particles smaller in dimensions than the filter pore size. However, airborne particles create negligible clogging since the electrostatic forces inhibit their penetration into the pore structure. Current plans include an attempt to determine the effect upon the sensitivity of the apparatus when pore size is varied. Initial tests have been conducted using a 1.2 μ pore size. Sample handling apparatus and handling techniques are being tested presently, and should be resolved soon.

Upon completion of these initial shakedown runs, samples will be disseminated into the elutriation chamber by means of a squeeze bottle, and allowed to settle on the surface of a coarse glass frit. A flow of prepurified nitrogen will then be introduced through the frit and the resulting aerosolized material caught on the millipore filter located at the top of the elutriation chamber.

This test has two main purposes. First, it attempts to simulate the environmental conditions evolving from a person walking through an area where the terrain denial agent has been disseminated, and secondly, has a good chance of developing into a typical quality control test, by establishing a minimum requirement in terms of percent of original sample caught on the filter. If the minimum requirement is met, the sample would be acceptable, if not, the sample would not be acceptable.

3.1.1 Description of Apparatus

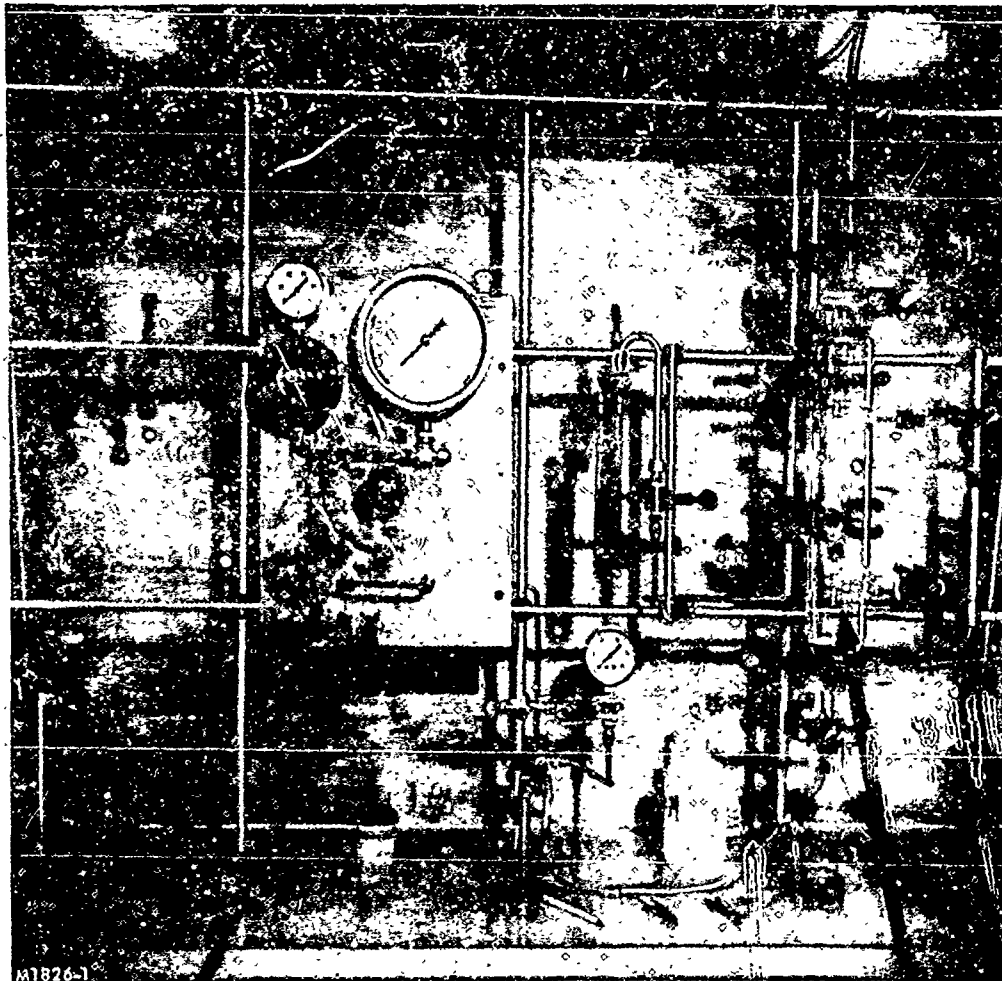
Basically, the apparatus consists of a pyrex glass tube 3 inches in diameter and 14 inches long. Laminar N₂ flow is maintained up the tube through utilization of a coarse glass frit located near the bottom of the tube. A two-way stopcock provides nitrogen entry into the tube and a means of draining off the decontamination fluid. Extremely accurate flow metering is achieved through four stages of regulation into a sapphire critical orifice flowmeter. Flow rate then becomes proportional to the upstream pressure. A photograph of the apparatus is shown in Figure 2.

3.1.2 Other Approaches

Objective examination of a new candidate reaerosolizability test is in progress presently. This test consists of a modification in the sample holder used for our sedimentation apparatus, to accommodate an intermittent metered gas flow. Here, we would use light attenuation techniques to determine a relative "reaerosolizability" comparison of samples by dispersing a small sample of agent onto a glass frit and then "puff" a volume of purge gas through the frit. The resulting aerosol cloud would then attenuate a monitored light beam. We would allow the sample to settle again, and then repeat the procedure several times. Resulting data should form a profile of light attenuation vs time, which would tend to level out. Hopefully, these data would reflect the ability of the sample to reaerosolize under time dependent conditions and also provide a relative relationship between various batch samples. Advantages of this approach include the adaption of one piece of test equipment in three characterization areas (reaerosolizability, particle size, hydrophobicity), this piece of apparatus being our sedimentometer.

3.2 Particle Size

There is an evident need for a simple, inexpensive particle sizing and counting device, particularly in the 1-10 μ range, which can be operated rapidly by personnel with a minimum



Nitrogen
Metering System

Elutriation
Chamber

Figure 2. Candidate Elutriation Apparatus.

of training. Since the measurement of particle size distributions involves the counting and size assessment of a large number of particles, at least 600-800 particles per sample must be examined in order for it to be statistically representative of the whole. Also, since the particles are usually randomly situated on the slide, it is difficult for the operator to remember which ones have been counted. Many devices have been developed for particle sizing processes including several fully automatic instruments. The fully automatic instrument, while having the advantage of speed of operation, also has some disadvantages such as those listed below.

1. Each particle must be separated from the other. The human operator can correctly record two particles in contact with each other, but the scanning type instrument usually cannot.
2. The sample used in the instrument must be free from foreign materials. The human operator, however, can distinguish foreign bodies due to their physical characteristics.
3. The electronic sizing devices now available require trained personnel for their operation.
4. These sizing devices are in general, rather expensive (\$3500 or more).

In concurrence with our task of developing quality control instruments which are simple, meaningful, and sensitive, a recent reference has been found which describes a semiautomatic instrument which has the potential of overcoming these possible problems and offers other attractive features (Ref. 55).

1. Accurate sizing is possible by personnel after only a minimum of training.
2. The operator may work the instrument from a comfortable position, using the eye for selection of particles and estimation of their size.

3. It will not be necessary to look away from the image in order to register the particle in the appropriate size category.
4. Size estimation is achieved by superimposition of standard size circles over the particle images. This technique is among the most accurate estimation techniques known, including standard optical microscope counts.
5. It is possible to indicate those particles which have already been counted.
6. It is a very fast method of particle counting and sizing.
7. It reduces operator fatigue to a minimum.
8. It works directly from a photographic negative.

3.2.1 Description of Apparatus

All specimens examined in the device are in the form of standard 35 mm negatives. The source of these can be either the electron or the optical microscope, thus giving a very wide range of application extending from 100Å to 100 μ . Figure 3 shows a schematic drawing of the apparatus. A 35 mm negative photograph of the sample is projected by a standard slide projector (Kodak Carousel 850) onto the underside of a sheet of tracing paper at bench level, via a front surface mirror. Projection of the negative is at constant magnification. The image is then seen by the operator from above by transmission through the paper. The spot projector above the table projects a spot of light downward on to the tracing paper. The diameter of the projected spot is changed by rotating an aperture disk, on which apertures of varying diameters are presented. The selected aperture is illuminated and its image focused on the tracing paper. The change of aperture size is controlled through a gear train by rotating a handle at bench level. The spot projection assembly is supported at a constant height, and is capable of scanning the tracing paper by moving the handle used to change aperture sizes. Also coupled to the gear train is a 12-position rotary switch which moves in

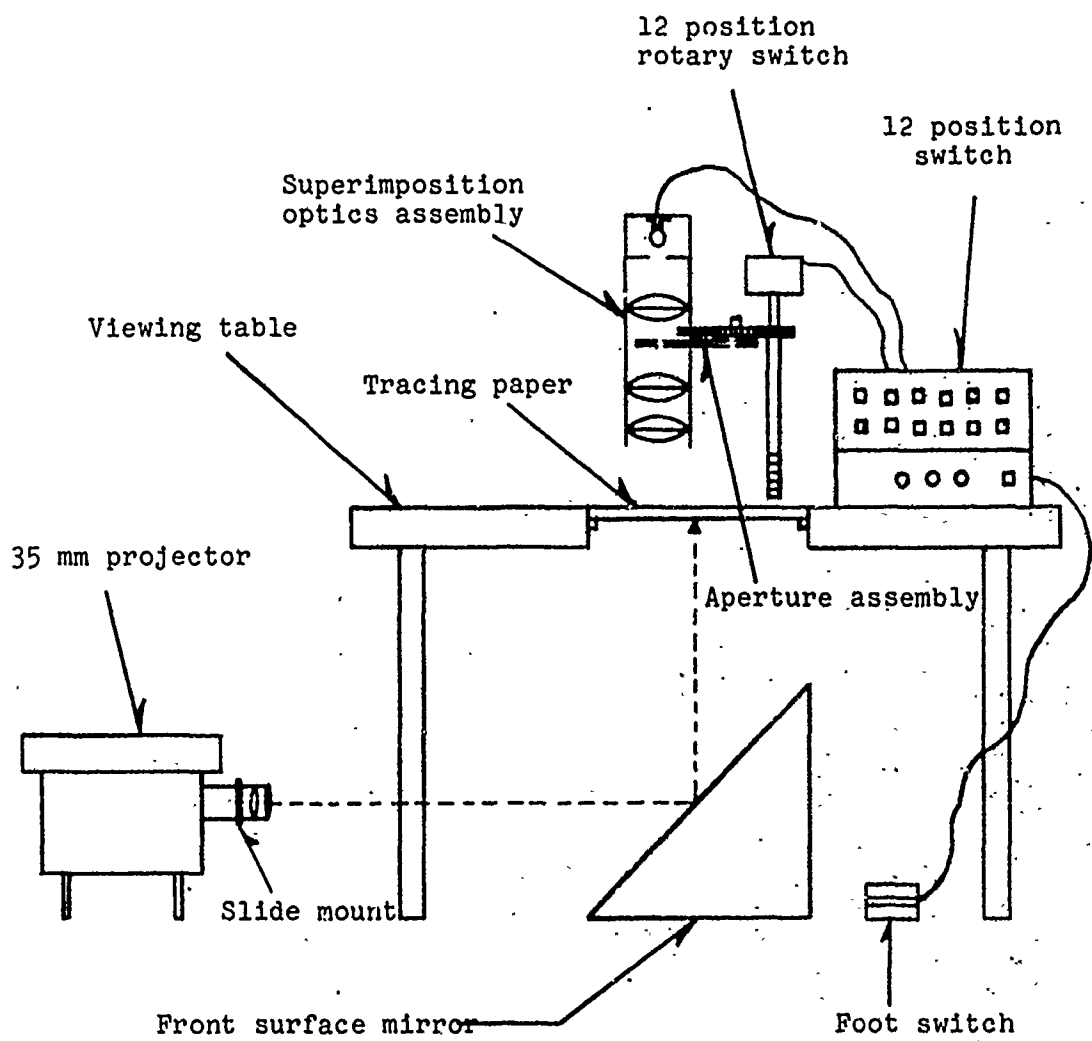


Figure 3. Schematic Diagram of Quality Control Particle Size Comparator.

synchronism with the aperture disk as the handle is rotated. The switch selects an appropriate electromagnetic register, corresponding to the size of the projected spot, and the operation of a foot switch adds one unit to that particular register. In use, the operator aims the projected spot on to the image of the particle to be counted, adjusts its diameter to approximately that of the particle image by rotating the handle, and then presses the foot switch. The use of tracing paper as the screen allows each projected particle to be marked by a pencil as it is counted, eliminating the possibility of double counting. The tracing paper is then replaced after each analysis. The diameters of the projected spots are a matter of individual requirement, the disks being replaced easily. For instance, if they were chosen to give evenly spaced points on the logarithmic scale used when plotting particle size distributions, an interval of a factor of $\sqrt{2}$ may be chosen. Thus, with an overall magnification of 7000, the particle size could extend from 0.2μ to 9.0μ in 11 logarithmically equal steps with an actual starting aperture size of 0.14 cm.

All commercially available portions of this apparatus have been received and fabrication is in progress. Methods of slide preparation will be investigated when measurements are started.

3.2.2 Other Approaches (Sedimentation)

A very simple version of a photo-extinction sedimentometer described by Rose (Ref. 55) has been developed under Task X of Contract DA-18-035-AMC-136(A). The photo-extinction method, based upon the determination of the opacity of a suspension of a given powder sample in a suitable dispersing fluid, offers advantages as a candidate quality control test as follows:

- (1) A good degree of accuracy is obtainable.
- (2) Sample size requirements are small.
- (3) A very large number of particles are examined (>10,000)

- (4) While data derivation is complex, instrument operation is very simple.
- (5) Microscopic techniques are not involved.
- (6) Apparatus is relatively inexpensive.

Along with these potential advantages, however, it is important to realize there are easily introduced errors that could render the apparatus unreliable.

Factors contributing to unreliability are as follows:

- (1) Lack of knowledge of the basic laws of transmission of light through a suspension.
- (2) Derivation of equation (2) postulates K_x as unity, when practically it deviates considerably from this value.
- (3) This method becomes highly inaccurate if flaky materials are present.
- (4) The particles must be absolutely opaque.
- (5) You must assume there is no reflection between the particles or between the particles and the walls of the vessel.
- (6) The solid angle subtended by the photosensitive particle surface must be small or scattered light will effect the photocell.
- (7) Thermal and vibrational effects can introduce large errors.
- (8) Changes in lamp intensity causes wavelength changes in spectral distribution which causes changes in photocell readout, necessitating frequent, accurate calibrations.

Bearing both these advantages and potential problems in mind, the following illustrates briefly some of the basic theoretical principles involved. Following Rose (Ref. 55), on the application of the photo-extinction methods to the analysis of powder size, you have a beam of light projected horizontally across a glass cell containing a suspension of the powder. The beam is at a distance H below the surface of the medium, and the vertical depth of the beam is h. The beam of light is projected through the suspension and falls upon a photocell.

Then under certain conditions the equation

$$\log_e \frac{I_0}{I_1} = kCl \sum \frac{d_x^3}{d^3} K_x n \cdot d_x^2 \dots \dots \dots (1)$$

holds, where I_0 and I_1 are the incident and emergent light intensities respectively; k, a factor depending on particle shape; C, the concentration of powder in gms/cc of suspension; l, the length of path; K_x , a factor relating the light-obscuring power of a small particle of diameter d_x to that of a similar particle, if the "square law" of geometrical optics is applicable; n, the number of particles of size d_x per gm of powder; and d , the diameter of the particles. If the particles are spherical

$k = \frac{\pi}{4}$, and, if it is assumed that $K_x = 1.0$, then $k \sum K_x n d_x^2$ is

the shadow projected area of the materials in the beam per gm of powder. The shadow projected area is then a quarter of the total surface area and, since $k \sum K_x n d_x^2$ is the shadow area per gm of powder, it is also a quarter of the total surface area per gm.

thus, we have

$$\frac{I_0}{I_1} = e \frac{ClS}{4} \quad (2)$$

where S is the specific surface on the exterior of the particles.

A more practical use for the apparatus might be to determine the size frequency of a powder. In this method, a sample of the powder is dispersed in the liquid medium and the ratio of the incident to the emergent light intensities is determined at known times through the period of the test. At any time t_2 , the diameter d_2 of the largest particle in suspension² in the beam of light will be that of the particle which has fallen the distance H in the time t_2 (all larger particles will have fallen clear of the beam)² and then this diameter may be calculated from Stokes' Law.

An approach such as the above, could be reduced to graphic form and simplified to conform to existing criteria for a quality control test.

3.3 Density

Initial measurements of apparent, bulk, and fluid densities of all samples on hand have been completed using the methods described below. Apparent density is defined as the weight of the powdered material divided by the volume it occupies when it is first placed into a container. Bulk density is found by dividing the weight of the powder by the minimum volume into which it can be compressed by vibration or tapping. Fluid density is found by dividing the weight of powder by its volume after it is shaken with air and allowed to settle to its maximum stable volume. The actual data are listed in Table 3. The close agreement of these numbers shows that these values are reproducible and that there is very little scatter in the data.

The average values of apparent, bulk, and fluid density for each of the powders tested are listed in Table 4. The weights of powder used were chosen in order to have volumes which could be read accurately in the apparatus used. It has shown that the densities measured are not influenced significantly by the sample size chosen. During the next reporting period, data interpretation will be undertaken through our statistical analysis program.

To date, no new or novel approaches to the measurement of densities have evolved. These reported data were gathered, using a graduated cylinder, in the following manner:

Table 3

DATA FOR DENSITY DETERMINATIONS ON CS POWDERS

<u>Sample Nomenclature</u>	<u>Fluid Volume (cc)</u>	<u>Apparent Volume (cc)</u>	<u>Bulk Volume (cc)</u>
CS-2-26 Sample wt - 3.74 gms	24	9.6	6.8
	21	10.0	6.8
	24	9.4	6.8
	24	10.0	6.8
	23	10.0	6.8
CS-2-28, #4 Sample wt - 2.52 gms	24	13.2	9.0
	25	13.2	9.0
	24	13.2	9.0
	25	13.8	9.0
	25	13.8	9.0
CS-2-28 (Bad?) by Fisher Sample wt - 3.38 gms	32	12.8	9.7
	35	12.8	9.7
	34	12.8	9.7
	34	12.9	9.7
	34	12.9	9.7
CS-1, #5 Sample wt - 5.95 gms	36	23.0	14.9
	37	22.8	14.9
	37	22.9	14.9
	38	23.0	14.9
	39	22.8	14.9
	38	23.0	14.9
CS-Beta Sample wt - 4.5 gms	34	13.4	7.9
	34	13.0	7.9
	38	14.0	7.9
	36	13.4	7.9
	36	13.4	7.9
	36	13.4	7.9
	36	13.4	7.9

Table 3 (Continued)

<u>Sample Nomenclature</u>	<u>Fluid Volume (cc)</u>	<u>Apparent Volume (cc)</u>	<u>Bulk Volume (cc)</u>
CS-2-26	16	13.8	9.6
Bad Lot - Northrup	15	13.0	9.6
Sample wt - 4.0 gms	16	13.0	9.6
	16	13.0	9.6
CS-Alpha	30	11.0	7.8
Sample wt - 2.88 gms	31	9.5	7.8
	31	9.0	7.8
	31	-	7.8
	31	11.0	7.8
CS-2-28 (lumpy)	24	13.0	10.0
Proc. Tech.	26	13.0	10.0
Sample wt - 4.84 gms	25	13.0	10.0
	24	12.5	10.0
	24	13.0	10.0
	24	13.0	10.0
CS-2-17 (Bad?)	57	24.5	15.0
Proc. Tech.	58	24.0	15.0
Sample wt - 5.32 gms	56	24.0	15.0
	59	24.6	15.0
	59	24.0	15.0
	59	24.0	15.0

Table 4

DENSITIES OF CS POWDERS

Sample Nomenclature	Apparent Density, gms/cc	Bulk Density, gms/cc	Fluid Density, gms/cc	Bulk-to- Fluid Density Increase, %
CS-2-28, #4	0.19	0.28	0.10	172
CS-2-17 (Bad?) Proc. Tech.	0.22	0.36	0.09	286
CS-1, #5	0.26	0.40	0.16	153
CS-Alpha	0.29	0.37	0.09	297
CS-2-28 (Bad?) by Fisher	0.30	0.40	0.11	250
CS-2-26 Bad Lot, Northrup	0.30	0.42	0.25	65
CS-2-26	0.31	0.55	0.16	246
CS-Beta	0.34	0.57	0.13	356
CS-2-28 (Lumpy) Proc. Tech.	0.37	0.48	0.20	144

3.3.1 Bulk Density

A weighed sample of the material was sealed in a graduated cylinder and various compaction motions tested to determine which would produce the smallest volume for a given sample. A Cenco rotational vibrator (Cenco-Meinzer Sieve Shaker, Catalog Number 18480) running at a setting of 6 on the rheostat was found to give the best results. Each sample tested was run several times and the values reported.

3.3.2 Apparent Density

Each sample was fluidized in the graduated cylinder by placing the cylinder in a horizontal position and rocking it slowly back and forth. The cylinder was then placed in an upright position and allowed to settle until no visible evidence of settling occurred. This procedure was repeated several times for each powder.

3.3.3 Fluid Density

Various motions of the graduated cylinder were tested to achieve maximum fluidization of the sample. Placing the graduated cylinder in a horizontal position and slowly rocking it back and forth produced the best results. The cylinder was then rapidly placed in an upright position and that volume where the sample showed visible evidence of forming a finite completely opaque cylinder of powder was taken as the fluid volume. These measurements were taken several times and the reported data reflect an average of the gathered values.

3.3.4 Bulk to Fluid Density Increase

Another property thought to be of possible significance is the percentage increase of bulk density compared to fluid density. These calculated data are reported in Table 4. The formula used for the calculations is as follows:

$$\text{Increase (\%)} = \frac{D_B - D_F}{D_F} \times 100$$

where D_B and D_F indicate bulk and fluid densities, respectively.

3.4 Flowability

3.4.1 Initial Methods Tested

Two candidate devices for measuring flowability have been tested, but both were unsuccessful. Both of these used small powder samples. One of these was shaped like an hourglass which had an orifice between the two halves approximately one millimeter in diameter and was fabricated from pyrex. Powder samples of 2 gms were placed in one half of the device, but the samples would not flow through the small orifice.

The other test was an inclined plane type test where we took two erlenmeyer flasks, cut off the necks, and connected them together so that the powder had a small circular trough through which to flow. Flow occurred in these tests, but the results were very erratic.

3.4.2 Funnel Test

Our present efforts to develop a flowability test are being concentrated on developing a test for rate of flow of fluidized powder through a vinyl funnel. Dry box apparatus capable of containing vinyl funnel flow tests is now near operation, and funnel flow tests will be conducted during the next reporting period.

3.4.3 Other Candidate Flow Devices

Two tests are being considered as candidate quality control instruments for the evaluation of powder flow characteristics. The first of these is the method of measuring the angle to which a mound of powder is inclined before flow begins. This piece of apparatus is in the final fabrication stage.

The other candidate flow test consists of using an hourglass shaped sample container which is loaded with a sample of powder and placed into a cylinder filled with water. This cylinder is then sealed tightly. The ends of the hourglass have concave geometry and when the cylinder is inverted with the sample contained in the top of the hourglass, the center of gravity changes causing the hourglass to tilt and lean

against the side of the cylinder. As the powder begins flowing through the hourglass orifice it collects on the concave surface of the lower compartment, causing the center of gravity to begin changing again. When a certain amount of sample has flowed into the lower compartment, the hourglass rights itself and begins to sink to the bottom of the tube. We may then compare the time required for this phenomena to occur on a relative basis between samples.

3.5 Hydrophobicity

The hydrophobic nature of the agent particle will determine to a large extent just how much effect water in any form (vaporized, adsorbed, or liquid) will have on availability of the agent in any natural environment in which water will certainly be present. The more hydrophobic the powder material is, the more readily it can be reaerosolized from a wet surface.

The classical method of determination of hydrophobicity is the measurement of the contact angle a drop of water makes with the surface of a pressed disc of the powder material. The method which in general is capable of yielding good results, is not a simple method and in several respects does not qualify as a quality control test. Skill is required to prepare a suitable disc of the material from which reproducible data can be obtained. In addition, equipment is rather specialized and requires a considerable amount of extremely careful work. The method is useful in the research laboratory, however, and, as such, would find use as a calibration method for other approaches.

Two methods have been chosen as possible quality control methods. These involve first, a modification of the Langmuir-Blodgett technique and second, a photosedimentation apparatus.

The first method, the modification of the Langmuir-Blodgett technique, involves placing a weighed quantity of the powdered material on the surface of water and measuring the area over which it spreads. In a hydrophobic material the forces of attraction between the particles would be much larger than the attraction for water and the area of spread would be relatively small. If however a more hydrophilic material of the same general type is spread on the surface, the attraction for the water would increase, and the area covered by the powder would be larger.

The apparatus to measure hydrophobicity by this technique has been assembled and is shown in Figures 4 and 5. The apparatus is relatively simple in that it could easily be duplicated in almost any laboratory. The camera equipment is not critical and while a Polaroid camera is desirable, almost any camera with a close-up lens could be employed. The sample tray and thermostat tray are shown in Figure 4. These are positioned on a light table, which in our case is an 8-inch square piece of frosted lucite mounted over two 24-inch fluorescent light fixtures. Both trays are constructed from lucite and in general the dimensions are not critical. The two ends of the sample tray are lower than the sides by $1/4$ inch so that there is a surface for the lid to rest on and to provide a method for cleaning the surface of the water with a notched plastic scraper. The lid of the sample tray contains a wire grid through which the spread sample is photographed. Two methods are thus available to determine the area of the spread film, (1) using a planimeter, or (2) counting the squares of the wire grid.

Figure 5 shows the entire experimental set up using a Polaroid Model 900 camera and a Series 5, +4 close-up lens. This combination permits the camera to be positioned about 8 inches above the sample tray and to just fill the entire picture area with the image of the sample tray. As this camera has an electronic exposure mechanism, only small adjustments are required on the exposure to obtain suitable contrast in the finished print.

During an experiment the thermostatic tray is filled and circulated with water maintained at constant temperature. Clean distilled water is poured into the clean sample tray to a level slightly above the ends of the tray. The plastic scraper is then pushed across the sample tray to clean the surface and lower the level to a constant height. If the surface of the water is not clean this can be accomplished by floating a material such as talc on the surface and rescraping the liquid surface. A weighted sample of the agent to be studied is placed on the surface and allowed to spread. The lid of the sample tray is lowered and when the spreading is complete, a photograph is taken through the wire grid. The area covered by the sample is measured and the result normalized to allow for slight variation in sample weights.

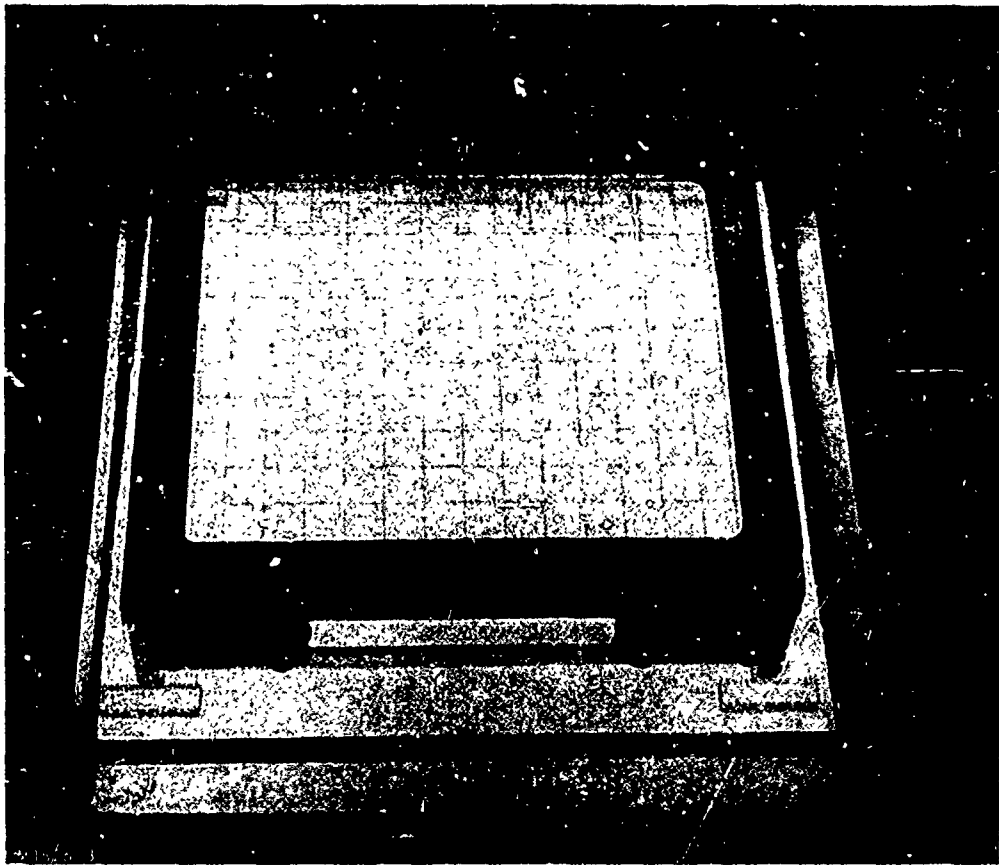


Figure 4. Hydrophobicity Apparatus Showing Thermostatic Tray and Sample Tray (with Wire Grid Cover) on Light Table.

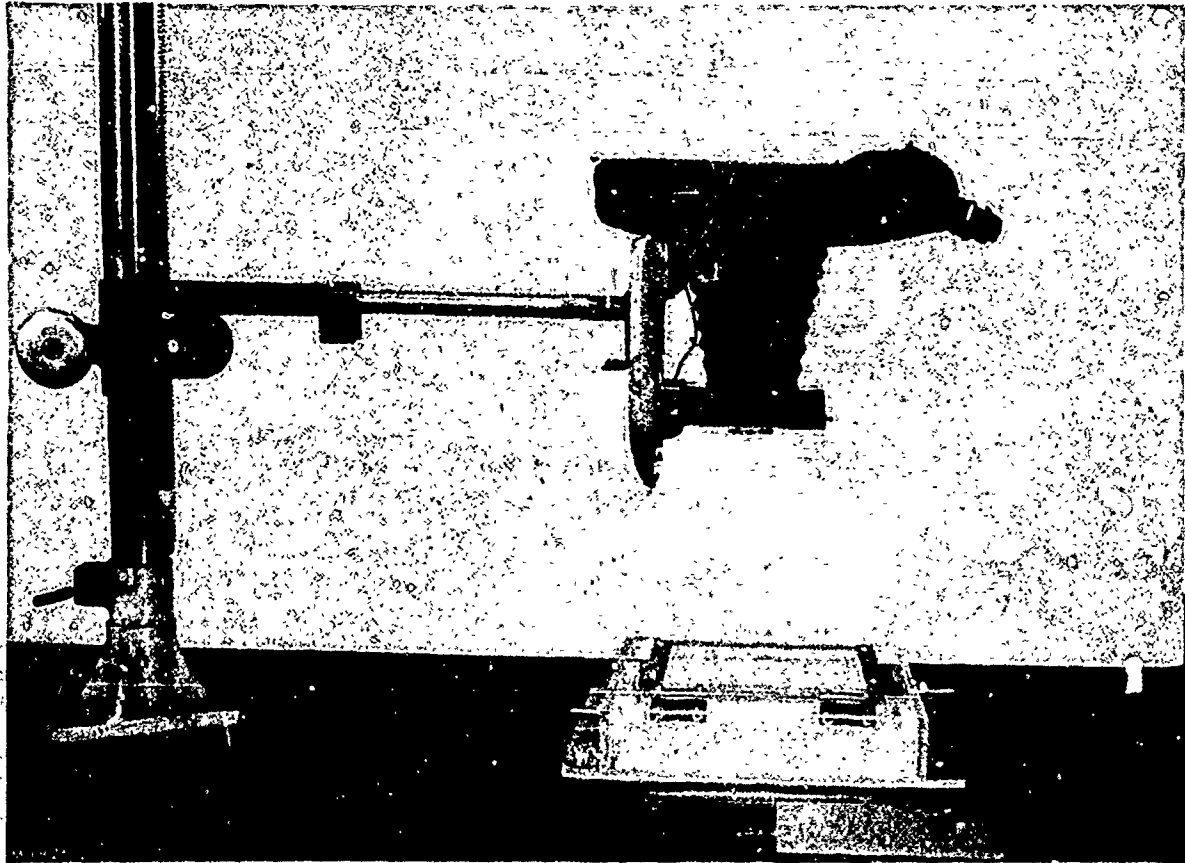


Figure 5. Hydrophobicity Apparatus - Complete
Experimental Apparatus.

As the equipment has just recently been completed, no data is available as yet on the various agent samples. All preliminary experiments as required for alignment, focusing and exposure variation have been carried out. The method should be capable of giving results indicative of the hydrophobicity of the sample, but as yet it is not known whether the method will provide sufficient sensitivity between various samples of a particular agent material. This will be established during the next report period.

The second method which appears to be capable of yielding information of the hydrophobic nature of the agents samples is a modification of the photosedimentation apparatus described previously. A weighed portion of the material will be suspended in a water medium in the photosedimentation tubes, using a sufficiently low concentration of the agent to permit the passage of the light beam through the sample while it is suspended. The tube is placed in the apparatus and the transmission through the tube at a specific height will be measured as a function of time. Several possible conditions could take place in the tube over a time interval. If the material is hydrophobic it would tend to resist any solubility effects, either to dissolve and possibly recrystallize which would tend to increase the particle size, or to be broken up by the water to form smaller particles. After a given elapsed time, the sample would be redistributed and rerun, and the second curve compared to the first. If the two curves are about the same, then no marked change has occurred in the particles. If the curves differ then it indicates that a change in particle size has occurred. It is anticipated that the relative differences in the two settling curves for various samples can be related and scaled to give a relative rating on the hydrophobicity of individual samples. By applying the same test to samples of known hydrophobicity, it would most likely be possible to calibrate the test.

3.6 Sintering

Sintering is the mechanism whereby mass migration of the material at ambient conditions causes small particles to agglomerate into larger ones. The other common mechanisms of agglomeration of particles at room temperature are usually associated with water, such as room. Since CS2 materials are hydrophobic these mechanisms would not be expected to be important in this case, but sintering might occur and so a test for it is needed.

A critical review of this area of study has indicated that any methods which involve storage of samples for a period of time does not truly fit with the requirements of a suitable quality control test which could be performed soon after a sample is manufactured and before it is shipped. As a result, attention has been diverted to other procedures which would tend to give a more immediate result. Sintering and agglomeration in general depends on the forces of adhesion between particles. The process of sintering is usually discussed in the terms of three stages: the first stage involves neck growth between particles and mechanical and cohesive bonding forces, the second stage involves diffusion and plastic deformation mechanisms, and the third stage involving the elimination of residual voids (Ref. 35). For our purposes the first of these is probably the most important.

The sintering of organic powder particles has been studied from a fundamental viewpoint in Task IX of Contract DA-18-035-AMC-136(A). It was found that the rate equations previously developed for sintering of metals and ceramics at high temperatures apply also to organic solids at room temperature. At ambient temperature and pressure the rate controlling process for crystalline powder sintering is evaporation-condensation, while the mechanism for amorphous powder sintering is viscous flow. An alternate mechanism for sintering, that of caking has also been fundamentally treated during the above-mentioned study. In this case, the caking reaction would most probably be an important agglomeration mechanism under storage conditions.

The development of a quality control test to determine the sintering ability of powdered agent materials is being approached in several ways. The first method under consideration is that of the particle bridging ability. It has been observed that flow appears to be influenced markedly by storage and further that flow rate changes with storage much sooner than other properties such as particle size, etc. This change in flow rate is most likely due to adhesions between the particles, stage one in the sintering of particles. Brown and Richards (Ref. 57) have investigated the flow of non-cohesive powders through orifices. Two important results were noted. The first is that the flow of solid through the orifice was independent of the head of solids above the orifice. The second was that blocked apertures could be obtained even when the operative diameter was 10 times the particle diameter. This is independent of the material of the orifice and can be found in vertical pipes. This restricted flow is characteristic of the bridging parameter of the particle, which is related to the cohesive forces and hence sintering ability.

A device will be constructed to measure the bridging ability of the series of agent samples. It will consist of a shallow box with a series of apertures of varying size. The box is filled with the material and the smallest aperture through which the powder flows will be observed and investigated to determine if it is a characteristic bridging parameter of the powder.

An alternative method for determining the sintering ability of a powder material would involve forming a packed bed of the material and measuring the flow through the bed, or the thermal conductivity of the bed. A standardized technique would be required to prepare the packed bed, which would involve a cold pressing technique. Both the measurement of flow through the bed and the thermal conductivity would depend on the pores in the bed which would relate to particle adhesion and sintering ability. The measurement of flow through the bed or permeability can be accomplished accurately and with good reproducibility using a manometer to measure pressure differences. A disadvantage of the method is that the results depend not only on porosity and method of compacting the sample, but on the particle size and particle size distribution. However, as these will be determined by other tests, the results should be correlative with the sintering ability of the powder.

The thermal conductivity through a packed bed depends on the voids in the packed bed which in turn depends on the adhesive forces between particles as well as the particle size and particle size distribution. The major contribution to the transfer of heat is the gaseous phase rather than the transfer by point-point contact of the particles. As the measurement of thermal conductivity is somewhat difficult, this method will not be utilized unless other methods are found to be undesirable for one reason or another.

3.7 Evaluation of CS Characterization Data by Statistical Analysis Methods

The goals of this subtask are to (1) determine which coated CS sample (out of a number coated CS samples produced under various process conditions and by a number of suppliers) is superior in performance and (2) what the critical physical

property values associated with the superior sample are. These are being investigated by statistical methods. A start is being made with the statistical evaluation of the sample data. These data consist of performance and physical property data such as:

- (a) funnel flow rate (mass and volume)
- (b) % elutriation
- (c) dissemination efficiency
- (d) 'Mity Mite' dispersion
- (e) apparent density
- (f) bulk density
- (g) fluid density
- (h) fluid/bulk density increase
- (i) particle size distribution

for any of the samples, under both dry and wet test conditions. Some of the performance parameters (for example, 'Mity Mite' dispersion) can only (or more readily) be expressed in a semi-quantitative manner, i.e. quality levels such as A, B, C ranking achieved by the order of the semi-quantitative values of the performance parameter.

The statistical techniques presently under consideration are:

1. Multiple linear regression to test for correlation between the performance parameters for which quantitative values exist and the totality of the physical property parameters.
2. Spearman rank correlation tests between the performance parameters for which only semi-quantitative values exist and any of the physical property values individually.

3. Linear regression techniques or Spearman rank correlation tests to test for correlation between the various performance parameters.

It is hoped that the application of these techniques will identify the coated samples characterized by an optimum value of an individual performance parameter. In the case that no correlation exists between two or more of the performance parameters, a trade-off study should be made to determine what sample has the most desirable combination of values of the performance parameters.

3.7.1 Evaluation of Semi-Quantitative Data

The semi-quantitative data on "Mitey Mite" dispersion and aerosol chamber decay was ordered according to a subjective quality index. Unfortunately, the nature of the measurements on which these rankings are based are such that only a limited number of quality gradations can be recognized. For example, "Mitey Mite" dispersion data could only be grouped in six categories and the aerosol chamber decay data only in four categories. Such small populations do not lend themselves to accurate evaluation by means of methods of nonparametric statistics. For example, Spearman rank correlation coefficients can be determined to test the hypothesis of positive correlation between the rankings according to "Mitey Mite" dispersion and the rankings according to apparent density, bulk density, fluid density, percentage of elutriation etc., but the small number of rankings ("observations") would not result in values characterized by high confidence levels. Another factor which would make the results of evaluation of the data at hand by means of a ranking method questionable, is that specific values of the variables to be associated with the "Mitey Mite" dispersion and aerosol chamber decay data must be chosen. Within the same ranks there exists considerable spread in the values of physical property and performance parameters. This spread is particularly large for the physical property values. Rankings based upon the physical property values and performance parameter values are thus somewhat arbitrary.

While it does not appear at this time as if meaningful correlations can be found between the semi-quantitative parameters and the quantitative parameters, we will continue

to search for some method for relating the "Mitey Mite" dispersion data and the aerosol chamber decay data to the other parameters.

3.7.2 Evaluation of Available Test Data

A preliminary study was made of the data collected by CRL on "wet" and "dry" samples of coated CS material. Quantitative data are available for:

1. Physical property parameters such as

- a. apparent density
- b. bulk density
- c. fluid density
- d. fluid/bulk density increase
- e. particle size

and for

2. Performance parameters such as

- a. funnel flow mass/unit time
- b. funnel flow volume/unit time
- c. % elutriation
- d. dissemination efficiency

Some considerations on the evaluation of semi-quantitative data are presented for the performance parameters:

1. "Mity Mite" dispersion and

2. Aerosol chamber decay

A preliminary evaluation was made which consisted of a multiple linear regression analysis of the data. To facilitate the large number of calculations necessary for this analysis, an existing IBM computer program for multiple linear regression analysis was adapted to this task. Appendix A shows a listing of this program. Calculations of the various statistical data were done for (a) all ("wet" and "dry") samples and (b) the "dry" samples, and (c) the "wet" samples.

The physical property parameters were selected as the independent variables in this analysis. The dependent variables were the performance parameters. Some of the results of this analysis are presented below in tabular form. Table 5 shows typical values for the correlation coefficients related to intercorrelations between the independent variables. Very poor correlation exists between the various density values and between the various density values and the fluid/bulk density increase. Tables 6, 7, and 8 show the correlation coefficients related to intercorrelation between the dependent variables and the independent variables. The following tentative conclusions can be drawn from these tables:

1. The correlation coefficients for all other data related to the performance parameters and the physical property values are not high, indicating that these data do not substantiate a close relation between these variables.
2. Very poor correlation exists between all other data related to the performance parameters and physical property values.

Table 5

CORRELATION COEFFICIENTS RELATED TO CORRELATION BETWEEN
INDEPENDENT VARIABLES FOR "DRY" SAMPLES

	<u>Apparent Density</u>	<u>Fluid Density</u>	<u>Bulk Density</u>	<u>Fluid/Bulk Density Increase</u>
Apparent Density	1.00	0.73	0.66	-0.41
Fluid Density	0.73	1.00	0.72	-0.65
Bulk Density	0.66	0.72	1.00	0.00
Fluid/Bulk Density Increase	-0.41	-0.65	0.00	1.00

Table 6

CORRELATION COEFFICIENTS PERTINENT TO ALL
("WET" + "DRY") SAMPLES

	<u>Apparent Density</u>	<u>Fluid Density</u>	<u>Bulk Density</u>	<u>Fluid/Bulk Density Increase</u>
Particle Size	-0.53	-0.61	-0.63	0.21
Funnel Flow (Mass)	0.78	0.81	0.88	-0.62
Funnel Flow (Volume)	-0.21	-0.61	-0.49	0.65
Percent Elutriation	-0.26	-0.44	-0.09	0.54
Dissemination Efficiency	-0.41	-0.41	-0.32	0.40

Table 7

CORRELATION COEFFICIENTS PERTINENT TO "DRY" SAMPLES

	<u>Apparent Density</u>	<u>Fluid Density</u>	<u>Bulk Density</u>	<u>Fluid/Bulk Increase</u>
Particle size	-0.61	-0.70	-0.64	0.28
Funnel Flow (Mass)	0.86	0.87	0.85	-0.65
Funnel Flow (Volume)	-0.37	-0.84	-0.65	0.62
Percent Elutriation	-0.10	-0.33	0.11	0.59
Dissemination Efficiency	-0.35	0.57	-0.15	0.56

Table 8

CORRELATION COEFFICIENTS PERTINENT TO "WET" SAMPLES

	<u>Apparent Density</u>	<u>Fluid Density</u>	<u>Bulk Density</u>	<u>Fluid/Bulk Increase</u>
Particle Size	-0.52	-0.51	-0.65	0.12
Funnel Flow (Mass)	0.74	0.76	0.94	-0.63
Funnel Flow (Volume)	-0.36	-0.42	-0.32	0.65
Percent Elutriation	-0.36	-0.52	-0.24	0.74
Dissemination Efficiency	-0.45	-0.28	-0.42	0.53

4. CONCLUSIONS

From this quarter's work we conclude:

1. Apparent, bulk, and fluid densities can be measured with a high degree of reproducibility by the methods described in this report.

2. Statistical analysis of Edgewood data on CS powders shows a possible correlation between apparent density and mass funnel flow, but all other combinations of apparent density, bulk density, fluid density, and bulk-to-fluid density increase with mean particle size, funnel flow, elutriation, and "Mity Mite" dispersion as measured at Edgewood do not appear to be closely related.

5. FUTURE WORK

Future plans for this contract include work to:

1. Finish the development of quality control tests to characterize CS-2 according to 1) reaerosolizability, 2) particle size, 3) flowability, 4) hydrophobicity, and 5) sintering.
2. Statistically analyze the correlation between these properties.
3. Prepare detailed descriptions of the most pertinent tests so that they can be used as quality control tests to offer guidance in the purchase and process development of CS-2.
4. Continue infrared studies of the surfaces of Cab-O-Sil HS-5 and Aerosil (model compounds) in order to better define their surface properties and characteristics.
5. Determine the mechanisms involved in the coating of powders with HMDS.
6. Coat powders with different types of coatings and correlate them with the results of pneumatic and explosive dissemination tests.

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APPENDIX A

TASK 5T

STATISTICAL ANALYSIS OF CS CHARACTERIZATION DATA

STATISTICAL ANALYSIS OF CS CHARACTERIZATION DATA

Program Description

The Multiple Regression Program used in these data analysis will accept a total of nine variables along with any combination of dependent and independent variables, up to thirty observations. The dependent variables are entered first on the data cards and the program iterates on them individually and in conjunction with the multiple independent variables. This is done by setting up a working array from the input array.

Four subroutines in our IBM Scientific Subroutine Package are used to obtain the required results. One of these subroutines sets up the arrays containing the intercorrelations among the independent variables and the intercorrelations of the independent variable itself. The first column of the first array contains the correlation of the first independent variable with itself; the first with second, etc. Thus, the second column contains the correlations of the second independent variable, etc. The second array contains the correlation of the dependent variable with the first independent variable; then with the second independent variable, etc. These are the primary results of this analysis. The program has as output, a first page containing input information and the input array, and two pages for each consecutive multiple regression.

1.

```

*LIST ALL
*IOCLCARD=1122 PRINTER1
*ONE WORD INTEGERS
DIMENSION A(20),X(10),S(30),R(AR),B(10),D(10),K(22),M(10),
I(6),T(1),I(1),S(1),R(1),L(1),M(1),R(1),S(1),A(1),T(1),D(1),B(1)
THIS MULTIPLE LINEAR REGRESSION WILL ACCEPT UP TO FIVE
INDEPENDENT VARIABLES AND A TOTAL OF NINE VARIABLES
THE INPUT FORMATS ARE 300 AND 301

READ(2,300)NDV,NV,NO,NC,MS
300 FORMAT(I5,I2)

N=NO
MID=NV-NDV
WRITE(3,400)NV,D,NDV,MID
400 FORMAT(10X,'N=NDV',10X,'NO OF VARIABLES=',10X,'NO OF OBS.',
10X,'NO OF DEP. VAR.',10X,'NO OF IND. VAR.',10X,'')

DO 10 I=1,NO
READ(2,301)I(A),J(J),M(M),
301 FORMAT(10X,'I=',10X,'J=',10X,'M=')
WRITE(3,401)I(A),J(J),M(M),NO)
401 FORMAT(10X,'I=',10X,'J=',10X,'M=')
10 CONTINUE

ICASE=1
NVAOT=MIDV+1
LOIND=NOV+1

15 CONTINUE

DO 120 KCV=1,NDV
*****
I=1
DO 20 I=1,NO,NC
S(I)=1
20 I=I+1
NO=KCV-1
A=0
I=1

DO 30 KNO=1,NO,NC
LKV=KNO+NDV
I=I+1
30 DO 40 KIDV=1,NO,NV
M(KNO+NDV)=KIDV-1
DO 40 IDVM=M+1,M+NO
I=I+1
40 CONTINUE
GO TO 45
45 I=I+1
GO TO 30
46 N=N+1
30 I=I+1

NOI=NO-N
I=1
41=1

DO 43 KNO=1,NO,NC
LKV=KNO+NDV

```

2.

```

I=I+1
40 N=LKV-(KNO-1)-NO*(KOV-1)
X(N)=A(LKV)
M(KNO+NO)=LOIND-1
M2=1
DO 70 IDVM=M+1,M+NO
I=IDVM-(KNO-1)-NO*(NOV-1)-NO*(FNC)
M2=M2+1
70 X(M)=A(IDVM)
M=M+1
AD I=I+1

WRITE(3,402)M,KOY,ICASE
402 FORMAT(10X,'M=KOV',10X,'ARRAY TO BE USED IN REGRESSION',10X,'M=',10X,'DE
PENDENT VARIABLE NO.',10X,'CASE NO.',10X,'')

N1=MVAOTM
DO 85 KNO=1,N
85 WRITE(3,403)KNO,I(K),J(K),M(K),N(K)
*****
CALL CORR(M,NVAOT,1,1,X,RAR,SID,DRX,R,SD,DI)
*****
WRITE(3,403)
403 FORMAT(10X,'RESULTS OF CORR',10X,'')

WRITE(3,404)I(KR),I(KI),I(KI),NVAOTI
404 FORMAT(10X,'MEANS',10X,'I(KR),I(KI),NVAOTI')

WRITE(3,405)I(KI),I(KI),NVAOTI
405 FORMAT(10X,'STD. DEVS.',10X,'I(KI),I(KI),NVAOTI')

WRITE(3,406)
406 FORMAT(10X,'SUMS OF CROSS-PRODUCTS OF DEVS. FROM MEANS',10X,'')

K1=NVAOT+2
DO 86 I=1,NVAOT
86 WRITE(3,407)IDR(I),I(KI),NVAOTI
407 FORMAT(10X,'I(KI),I(KI),NVAOTI')

WRITE(3,408)
408 FORMAT(10X,'CORRELATION COEFFICIENTS',10X,'')
K1=0
DO 88 I=1,NVAOT
DO 87 J=1,I
K1=K1+1
87 I=I+1
88 WRITE(3,407)IDR(I),I(KI),NVAOTI

WRITE(3,409)I(KI),I(KI),NVAOTI
409 FORMAT(10X,'DIAGONAL OF THE MATRIX OF SUMS OF C-PS OF DEVS. FROM
MEANS',10X,'I(KI),I(KI),NVAOTI')

DO 90 I=1,NVAOT
K1=1
90 I=I+1

CALL M-HERM(NVAOT,R,1,MIDV,SAVE,DRX,RTI)
*****
WRITE(3,410)

```

3.

```

410 FORMAT(10X,'OUTPUT FROM ORDER',10X,'INTERCORRELATIONS AMONG
INDEPENDENT VARS.',10X,'')

K1=NIDV+2
DO 100 I=1,NIDV
100 WRITE(3,411)IDR(I),I(KI),NIDV

WRITE(3,411)IDR(I),I(KI),NIDV
411 FORMAT(10X,'INTERCORRELATIONS OF INDEPENDENT VARS. WITH DEPENDEN
T VARS.',10X,'I(KI),I(KI),NIDV')
*****
CALL MINVIDR(NIDV,DI,MI)
*****
WRITE(3,412)
412 FORMAT(10X,'OUTPUT FROM MINV',10X,'INVERSE OF INTERCORRELATIONS
AMONG IND. VARS.',10X,'')

DO 110 I=1,NIDV
110 WRITE(3,407)IDR(I),I(KI),NIDV

CALL MULTR(NIDV,SBAR,STD,S,DRX,RV,SAVE,RC,SD,T,AHS)
*****
WRITE(3,413)I(KI),I(KI),NIDV
413 FORMAT(10X,'OUTPUT FROM MULTR',10X,'REGRESSION COEFFICIENTS',10X,'
I(KI),I(KI),NIDV')

WRITE(3,414)I(KI),I(KI),NIDV
414 FORMAT(10X,'STD. DEVS. OF REGRESSION COEFFICIENTS',10X,'I(KI),I(KI),
NIDV')

WRITE(3,415)I(KI),I(KI),NIDV
415 FORMAT(10X,'T-VALUES',10X,'I(KI),I(KI),NIDV')

WRITE(3,416)I(KI),I(KI),NIDV
416 FORMAT(10X,'INTERCEPT',10X,'MULTIPLE CORRELATION COEFFICIEN
T',10X,'STD. ERROR OF ESTIMATE',10X,'SSAR',10X,'DEGREES OF FREEDOM',10X,'
DEGREES OF FREEDOM',10X,'MEAN SQUARE OF SSAR',10X,'SSDR',10X,'DEGREES OF FREEDOM ASSO. WITH SSAR',10X,'ME
AN SQUARE OF SSDR',10X,'F-VALUE',10X,'')

120 CONTINUE

IF(ICASE=2)130,140,150

130 NC=2
MS=1
ICASE=ICASE+1

GO TO 15

140 NS=2
ICASE=ICASE+1

GO TO 15

150 CALL EX2

```

GLOSSARY

<u>SYMBOL</u>	<u>PARAMETER IDENTIFICATION</u>
A	Storage for NV variables and number of observations
ANS(1)	Intercept
ANS(2)	Multiple correlation coefficient
ANS(3)	Standard error of estimate
ANS(4)	Sum of squares attributed to regression
ANS(5)	Degrees of freedom of above item
ANS(6)	Mean square of same
ANS(7)	Sum of squares of deviations from regression
ANS(8)	Degrees of freedom of above
ANS(9)	Mean square of same
ANS(10)	F-Value
B	Diagonal of the matrix of the cross-products of deviations from means
B	Regression coefficients
CORRE	Subroutine to calculate the following values
DRX	Sums of cross-products of deviations from means
DRX	Intercorrelations among independent variables
KDV	Dependent variable index
LKDV, IKDN	Location of observation in "A" array
LOIND	Location of the first independent variable in "A"
MI, NI	Resulting location of observation in "X" array

MINV Subroutine to calculate the inverse of inter-correlations among independent variables; uses DRX

MULTR Subroutine to calculate the following values

N Number of observations less those containing zero

NC 1 entered, program used all observations.
2 entered, program used half of the observations

NDV Number of dependent variables

NIDV Number of independent variables

NO Number of observations

NS 1 entered, program uses odd observations
2 entered, program uses even observations

NT Total number of values entered

NTX Total numbers of values in "X" array

NV Total number of variables

NVAOT Number of variables at one time (NIDV + 1 dependent variable)

ORDER Subroutine to calculate the following values

R Correlation coefficients

RY Intercorrelations of independent variables with dependent variables

S Working storage to reject missing data (zeros)

SB Standard deviations of the regression coefficients

STD Standard deviations

T T-Values

X Array to be used in regression

XBAR Means

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) MONSANTO RESEARCH CORPORATION Dayton Laboratory Dayton, Ohio 45407		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE STUDIES OF SURFACE CHEMISTRY OF SOLIDS IN DISSEMINATION			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) First Quarterly Progress Report - August-October 1967			
5. AUTHOR(S) (First name, middle initial, last name) Hedley, W. H., Fearheller, W. R., Jr., Richardson, G. A., and Zanders, D. L.			
6. REPORT DATE February 1968	7a. TOTAL NO. OF PAGES 72	7b. NO. OF REFS 57	
8a. CONTRACT OR GRANT NO. DAAA-15-68-C-0006	8b. ORIGINATOR'S REPORT NUMBER(S) QPR-1, MRC Project No. 4530		
8c. PROJECT NO. Task No. 1B522301A08101	8d. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010.			
11. SUPPLEMENTARY NOTES Chemical agent dissemination		12. SPONSORING MILITARY ACTIVITY Edgewood Arsenal Research Laboratories Edgewood Arsenal, Maryland 21010 (J. D. Wilcox, Ext 4512, Proj 0)	
13. ABSTRACT The objectives of this program are (1) to develop quality-control tests for CS-2, which will insure that the product that is accepted will be reaerosolizable and (2) to study the surface chemistry of powders to determine which factors limit their dissemination by pneumatic and explosive means. Quality-control-type tests are being developed on CS powders for (1) reaerosolizability, (2) particle-size distribution, (3) density, (4) flowability, (5) hydrophobicity, and (6) sintering. Reproducible data on apparent density, bulk density, and fluid density have been collected for CS powders. Statistical analysis of previously existing data on density, particle size, funnel-flow rate, elutriation, and dissemination efficiency for both wet and dry samples do not show a strong correlation, except for the case of bulk density and funnel flow rate. This analysis is continuing as new data are becoming available from this program. Preparation of surface coatings to apply to powders to determine their effect upon dissemination efficiency and the mechanisms which limit it has been started. A pneumatic aerosol dissemination chamber is being installed to provide a facility for testing these coated powders.			

DD FORM 1473 1 NOV 65

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Density Sintering Elutriation Particle size Flowability Dissemination Hydrophobicity Coating formulation Tunnel-flow rate Reaerosolizability CS characterization data Literature survey, powders Aerosol dissemination chamber						

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