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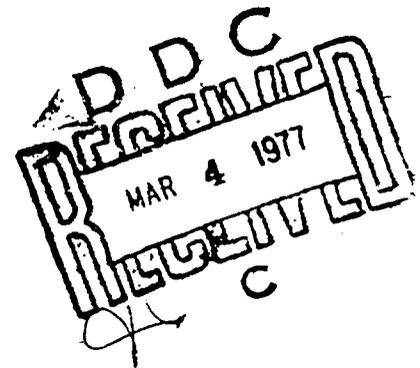
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Investigation and Development of Methods to Increase the Dispersibility of Aluminum Metal Powder

K.P. QUINLAN
J.J. HUTTA



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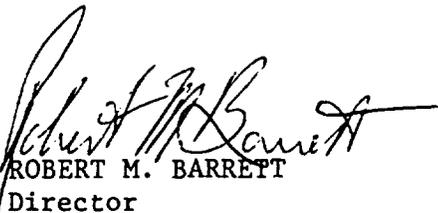
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20. (Cont)

Tullanox-500, and surface treatment of the aluminum spheres with water followed by drying with acetone.

Tests performed by MIT Lincoln Laboratory showed that these treated aluminum powders could be ideally dispersed with no subsequent agglomeration.

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Investigation and Development of Methods to Increase the Dispersibility of Aluminum Metal Powder

I. INTRODUCTION

The Optical Countermeasures Group of MIT Lincoln Laboratory has demonstrated that spherical aluminum particles in the micron size range will produce a distinct optical signature in the LWIR spectral region. However, in the course of early tests it was observed that the observed optical signature intensity was considerably less than predicted from Mie scattering theory. This was determined to be due to incomplete and nonuniform dispersal of the particles caused by agglomeration or clumping and necessitated a dispenser designed to overcome this difficulty. The point of departure of the experimental program reported herein is based on the thesis that if particle agglomeration is eliminated or significantly diminished at the outset, the aluminum powder may be effectively dispersed using a dispenser of relatively simple design.

Aluminum particles in the micron size range agglomerate by weak interaction to form clusters. These clusters usually exhibit a size greater than $35\ \mu\text{m}$. Interactions of this type arise from nonspecific attractive forces which can usually be described in terms of van der Waals forces and electrostatic attraction. Aggregation of aluminum particles may also involve small contributions from metallic as well as hydrogen bonds. Figure 1 is a scanning electron micrograph of the as-received aluminum powder and serves to give some idea of the nature and extent of

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agglomeration. The attractive forces between two particles can be described by the following relationship derived by Bradley,¹

$$F = A \frac{d_1 d_2}{d_1 - d_2},$$

where A is a constant independent of the dimensions of the spherical particles and d_1 and d_2 represent the diameters of the two solid spheres. A encompasses the number of attracting atoms on the spheres, van der Waals constant, and the distance between the centers of the surface molecules or atoms of the two spheres. Electrostatic forces are considered to be a minimum in this size range.² In similar studies,³ electrostatic contributions were found to be less than 9 percent.

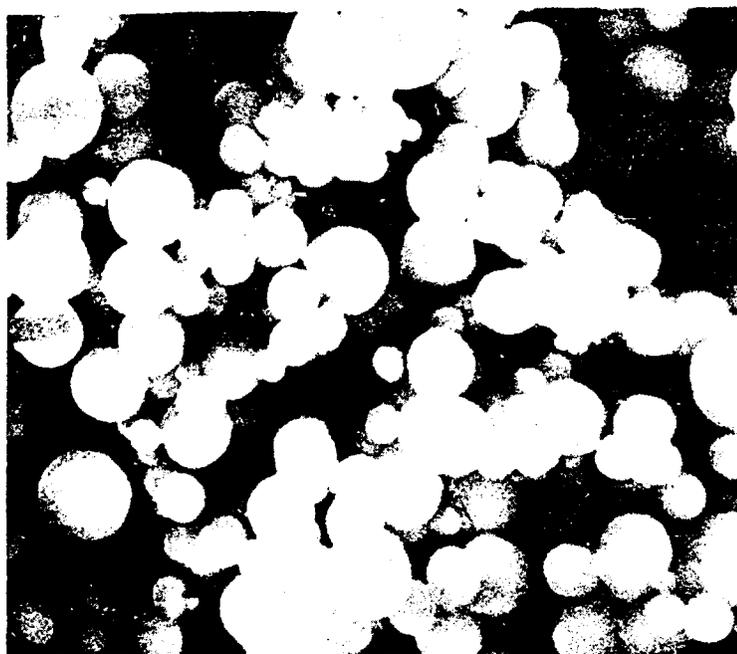


Figure 1. Scanning Electron Photomicrograph of the Aluminum Particles Used in the Present Study (mag. 3000X)

1. Bradley, R.S. (1932) LXXIX. The cohesive force between solid surfaces and the surface energy of solids, Phil. Mag., 13:853-862.
2. Kunkel, W.R. (1950) The static electrification of dust particles on dispersion into a cloud, J. Appl. Phys., 21:820-832.
3. Bohme, P., Hohn, P., Krupp, H., Rabenhorst, H., Schnabel, W., and Walter, G. (1973) Adhesion of gold particles to silicon and gold substrates in ultra-high vacuum, J. Appl. Phys., 44:3914-3918.

Although molecular or van der Waals forces are generally considered to be weak forces, they can nonetheless be considerable between micron sized particles at very short distances. Evidence of this is provided by the Lincoln Laboratory observation that aluminum powder dispensed from an evacuated canister exhibits a greater agglomerative tendency than powder that has not been subjected to vacuum treatment. It is possible that removal of naturally adsorbed atmospheric gases enhances interparticle attraction by permitting closer contact. Since it appears that prevention of agglomeration may be a matter of shielding one particle from another, we have taken three approaches to produce this condition:

- (1) Addition of free-flow solids which act through their spacing and lubricating properties to reduce agglomeration,
- (2) Coating the particles with polymers or materials which give the aluminum particles low-energy surfaces,
- (3) Decreasing the surface energy of the aluminum particles by modifying their surfaces by chemical means.

The investigation resulted in the development of three methods for increasing dispersibility. These are: the addition of activated carbon particles, addition of Tullanox-500 fumed silica, and modification of the aluminum particle surfaces by controlled oxidation. Coating of the aluminum spheres with polymers and hydrophobic materials for the most part proved ineffective. Teflon did exhibit acceptable dispersibility. Further research on the teflon study should be pursued in order to fully evaluate this approach.

2. EXPERIMENTAL

To ensure that our results would be directly applicable to the Lincoln Laboratory agglomeration problem, the aluminum powder used in these experiments was obtained from the same source (Valimet, Inc., Stockton, California) and subjected to size separation or classification procedure by the same processor (Donaldson Co., Inc., Tulsa, Oklahoma). The spherical particles are formed by atomization of molten aluminum in a helium gas jet. A 2 to 5 μm fraction was separated from the production-run powder with the use of an Acucut particle classifier.

Figure 2 gives the results of a size analysis of this cut using the Coulter technique. Plotting cumulative percentage frequency against particle size shows that 81 percent of the particles are between 2 and 5 μm in diameter. In order to perform this analysis the powder was dispersed in a 2 percent sodium chloride solution containing a dispersing agent. Otherwise, the powder is so badly agglomerated that a meaningful determination of ultimate particle size cannot be made.

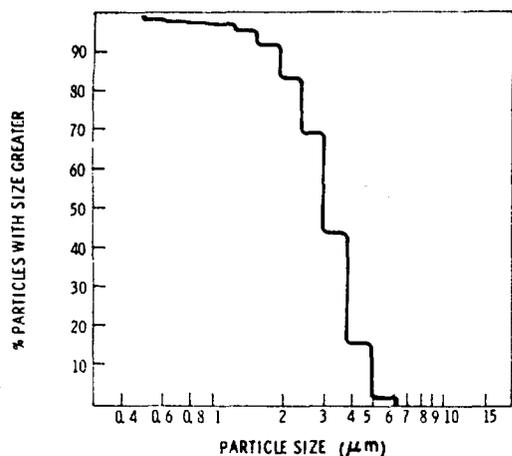


Figure 2. The Cumulative Percentage Frequency Curve Determined by the Coulter Counter. Median diameter = 3 μ m

Evaluation of the deagglomeration treatments was accomplished using three methods. Initial evaluation of the results of the various treatments was performed by visual observation of the free-flow character of the powder. If this test showed that a reasonable degree of deagglomeration had been achieved, the powder was further evaluated by sieve analysis.

In the early phase of the investigation, the elutriation method was tried as a measure of deagglomeration. The elutriation apparatus is shown in Figure 3. The method consists of flowing nitrogen or argon gas into the powder sample container attached to the base of the tube and measuring the weight of the powder carried away at designated pressure settings over specific intervals of time. For example, it was observed that 92 percent of a sample of the aluminum powder containing 18 percent of an activated carbon additive was carried away from the sample chamber at 33 psi nitrogen after 1 hr; whereas only 52 percent of the untreated aluminum was carried away at the same pressure in two hours. This method of evaluation, however, was discontinued after the initial phase of the investigation when it was determined that sieve analysis was a much more precise approach.

The sieve analyses were performed with the use of a model L3P Allen-Bradley Sonic Sifter fitted with a set of precision sieves consisting of 63, 37, 20, and 10 μ m sieves. Particles less than 10 μ m in diameter were received in the fines collector. The quantity of powder received in the collector is a criterion of the effectiveness of the deagglomeration treatment. The greater the quantity of powder passing the 10 μ m sieve, the better the deagglomeration treatment was rated.

The results of the sieve analyses are presented in graphic form, with sieve size in microns as the abscissa and the percentage of particles less than a given sieve size as the ordinate.

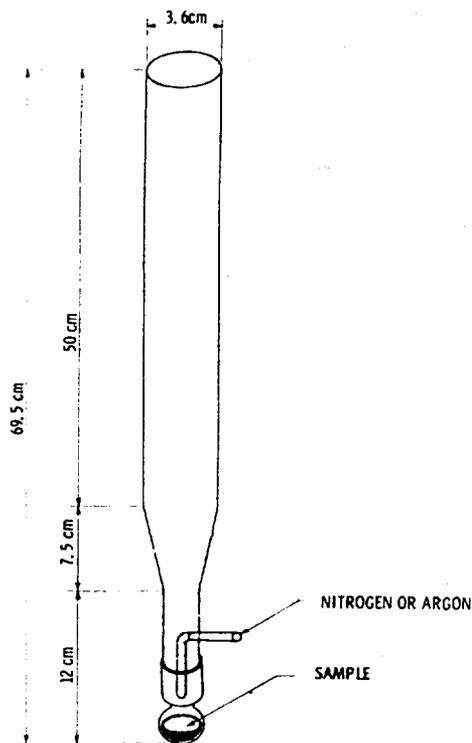


Figure 3. Air Operated Elutriator

The techniques used in our attempt to transform the aluminum powder to a useful agglomerate-free condition are described under the three separate experimental approach categories in Sections 2.1, 2.2, and 2.3.

2.1 Additives

Particulate solid additives were introduced in measured quantities ranging from 1 to 50 percent and distributed uniformly throughout the powder sample by mechanical tumbling and agitation. As a first-cut approach, several forms of fumed silica, a material used in commercial practice to impart free-flow characteristics to powders, were investigated. Later on, various types of particulate carbon and other powdered materials such as teflon and vanadium pentoxide were studied. The rationale for selection of this approach is that the additive particles will act as spacers to prevent large-area contact between the aluminum particles, thereby eliminating or significantly reducing the forces responsible for agglomeration. If the spacer particles are considerably smaller than the aluminum particles, the areas of contact will be small, and forces of attraction between the aluminum and additive particles will be correspondingly weak; providing no electrostatic forces are generated, and the additive does not readily adsorb water vapor from the atmosphere.

The candidate additive materials were subjected to rapid exploratory testing to identify those having the greatest potential as deagglomerating agents. These were then investigated in greater detail to establish optimum amounts required.

The possibility of coating the spherical aluminum particles with fumed silica and carbon in a high velocity jet mill was also investigated but found to be unsatisfactory. The jet mill used was a four-inch Micron Master Jet Pulverizer, Model 04-503 (The Jet Pulverizer Co., Merchantville, New Jersey). Results showed that the components were separated in the impact chamber with no significant coating having occurred. Separation was caused by the large density difference between the aluminum and the additives.

2.2 Coatings

In order to determine whether application of a low surface energy coating to the spherical aluminum particles would be effective in preventing agglomeration, a number of different experimental approaches and coating materials were investigated. Compounds likely to have desirable properties are found among low molecular weight organics, various polymers, and high molecular weight organic substances.

2.2.1 LOW-MOLECULAR WEIGHT ORGANICS

The coating of the aluminum spheres with low molecular weight organics was carried out either by evaporating a suspension of the organic with the Al or applied directly to the spheres from the vapor phase. In the latter case, the organic was passed through an aluminum bed using the apparatus shown schematically in Figure 4a. The organics studied were isopropanol, dimethylformamide, acetone, and dimethylsulfoxide. The dimethylformamide was selected because of its high dipole moment and low dielectric constant.

2.2.2 POLYMERS AND HIGH MOLECULAR WEIGHT SUBSTANCES

Coating of the aluminum spheres with polymers or high molecular weight substances was carried out in two ways: (1) application of a solution or suspension (teflon) of the polymer or high m.w. substance to the aluminum spheres with subsequent evaporation of the vehicle, and (2) photopolymerization of a monomer in the presence of the spheres.

The amount of the high M.W. substances required to give a monomolecular layer was calculated in the first approach. The polymers and high m.w. substances studied were teflon (Dupont, DLX-6000), stearic acid (Central Scientific Co.), polyethylene glycol (m.w. -600), Matheson, Coleman & Bell), polyethylene glycol (m.w. -3000-3700) Matheson, Coleman & Bell), styrene (Eastman Organic Chemical), and acryloid B72-100 percent (Rohm & Haas). The solvent-substance pairs were the

following: stearic acid-isopropyl alcohol, stearic acid-dioxane, stearic acid-benzene, polyethylene glycols-isopropyl alcohol, acryloid-dimethylformamide, styrene-n-heptane, teflon-acetone, and teflon-triethyl phosphate. In the case of teflon, small amounts of teflon (DLX-6000) were added to the solvent to form a suspension and this was followed by the addition of the aluminum particles. Following evaporation of the solvent, the free-flow character of the resulting powder was observed.

Three different experimental arrangements were investigated for the photopolymerization of monomers on aluminum spheres. These are shown schematically in Figure 4. The monomers studied were hexachloro-1, 3-butadiene (K&K Labs.) and tetrafluoroethylene (K&K Labs.). In each experiment the vapor of the monomers was either passed through or over the aluminum spheres. In the case of hexachloro-1, 3-butadiene, the vapor was carried by nitrogen or argon. The UV light source was a General Electric air-cooled B-H6 mercury lamp. The duration of irradiation was usually in the 1- to 3-hr range. In one experiment the aluminum spheres were coated with styrene prior to irradiation.

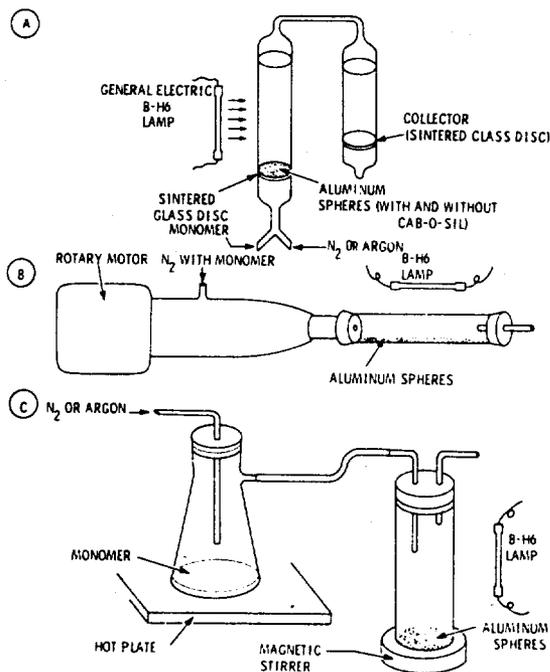


Figure 4. Apparatus Employed for the Photopolymerization of Monomers on the Surfaces of Aluminum Spheres

2.3 Surface Modification

This approach to deagglomeration was to modify the surfaces by chemical means in order to reduce the surface energy. Two methods were investigated to change the surface of the aluminum. The first method was to react the hydroxyl groups of the aluminum surface with hexamethyldisilazane. The hydroxyl groups possibly contribute to the agglomeration of the aluminum particles through the formation of hydrogen bonds. Twenty-four grams of aluminum in 80 ml of petroleum ether were treated with 15 ml of hexamethyldisilazane (Polysciences, Inc.). This solution was refluxed for 1 hr and then 2 ml of 1-propanol added. The mixture was filtered and the aluminum washed with petroleum ether and 1-propanol. The aluminum was given a final wash with petroleum ether. The product was then dried on a steam bath in a nitrogen atmosphere.

The second method was to treat the aluminum surface with water. The aluminum particles were allowed to remain in contact with the water at room temperature for thirty hours. The same effect could be attained in a shorter time by heating the mixture gently for approximately 1/2 hr and allowing the mixture to react overnight. It was also observed that hydrochloric acid produced the same result. The water-treated aluminum was either directly air-dried or subjected to several acetone washings to extract the treatment water and then dried in a thin layer in a large-area tray. The directly air-dried aluminum formed a hard cake due to oxide bridging of particles and required moderate grinding to reduce the resulting aggregates to a powder. The aluminum was processed into a fine powder by gentle tapping with a pestle. On the other hand, the acetone treated aluminum dried to a free-flowing condition requiring no grinding or further processing and was a far superior product.

3. RESULTS AND DISCUSSION

The results and discussion are given under the following separate titles in Sections 3.1, 3.2, and 3.3.

3.1 Additives

The first-level evaluation of all additives was based on visual observation of the slumping or flow characteristics of the powder mixture. The ratings assigned to the various additives are presented in Table 1.

Table 1 shows that four additives were found to give superior free-flow character to the aluminum powder: activated carbons, Cab-O-Sil (Cabot), Micro-Cels (Johns-Manville), and Tullanox-500 (Tulco, Inc.).

Table 1. The Effect of Additives on the Free-Flow Character of Aluminum Powder

Substance (%)	Eval. (⊕)	Substance (%)	Eval. (⊕)	Substance (%)	Eval. (⊕)
Activated Carbons*	††	Magnesium Fluoride (1.6, 15%)	†	Stearic Acid (20%)	-
Al ₂ O ₃ (5%, 20%)	-	Magnesium Oxide (1.7, 17%)	-	Talc (20%)	-
Cab-O-Sil*	††	Manganese (10%)	-	Teflon-7A (24%)	-
Carbon Blacks (20%) ^a	-	Micro-Cels* (20%)	††	Teflon-6 (20%)	-
Cinchonine (21%)	-	Molybdenum Sulfide (8%)	-	Teflon DLX-6000 (20%)	-
Anthraquinone (20%)	-	Platinum Black (14%)	-	Tullanox-500*	††
Lycopodium (5%, 20%)	-	Silver Powder (10%)	-	Thorium Oxide (10%)	-
Magnesium (10%)	-	Sodium Oleate (50%)	-	Vanadium Pentoxide (19%)	-

⊕ Evaluation: †† good dispersibility, † moderate dispersibility, - no improvement.

* These entries are discussed fully in the text.

a The carbon blacks evaluated were Mogul-L(Cabot), Sterling MS(Cabot), Carbolac-2(Cabot), and Japanese Kreha.

Activated carbons from different sources were observed to impart different degrees of free-flow character to the aluminum powder. Therefore a special effort was undertaken to obtain a number of activated carbons from different sources to find the most effective material commercially available. Activated carbons from Allied Chemical & Dye Corp. (Baker & Adamson, Code 1551), J. T. Baker Chemical Co., ICI United States Inc. (Darco), and Mallinckrodt Chemical Works were evaluated by elutriation or sieve analyses using electroformed nickel sieves with the sonic sifter. The activated carbon from Allied Chemical & Dye Corp. designated as Baker & Adamson, Code 1551, exhibited qualities superior to the other activated carbons studied. Figure 5 shows the sieve analysis of an aluminum-20 percent activated carbon (B&A) mixture where 58 percent of the mixture was observed

to have a particle size of less than $10\ \mu\text{m}$. When the untreated aluminum powder is sieved (Figure 5) less than 1 percent of the particles are found to have a size lower than $37\ \mu\text{m}$. Apparently the particles agglomerate into aggregates with diameters equal to and larger than $37\ \mu\text{m}$. Sieve analysis of the activated carbon alone shows that less than 2 percent of the particles have a size equal to or less than $10\ \mu\text{m}$. Thus, the carbon particles, too, form aggregates, but not to the same extent as the aluminum. Figure 5 clearly demonstrates that the addition of activated carbon to the aluminum powder greatly increases the dispersibility of the aluminum. Mixtures containing 13 percent or more of activated carbon have similar free-flow characteristics.

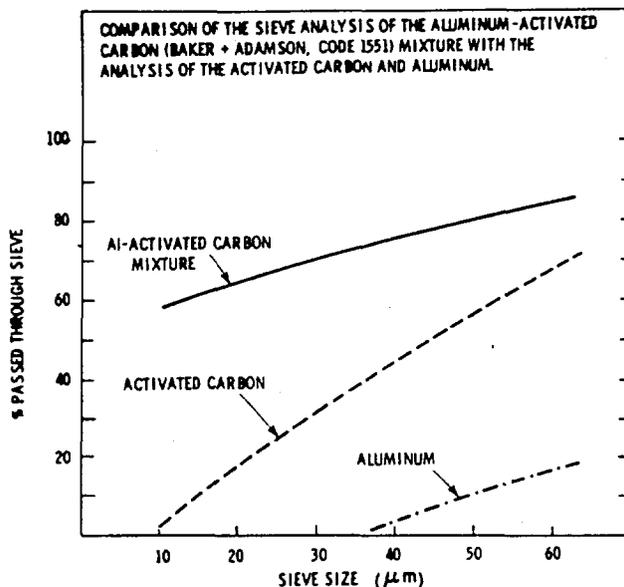
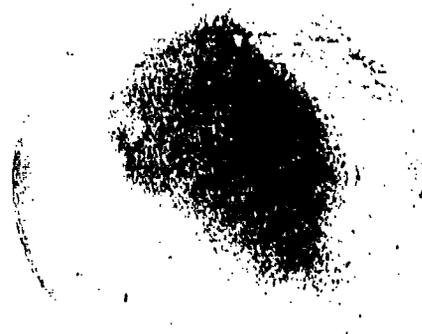


Figure 5. Size Analyses of (1) Aluminum, (2) Activated Carbon, and (3) Aluminum-Activated Carbon (20 percent) Mixture. Activated carbon is the Baker & Adamson, Code 1551, distributed by Allied Chemical & Dye Corp. Ordinate represents the percent of particles below the sieve size. The size analyses were performed with an Allen-Bradley Sonic Sifter (Model L3P)

The powder fractions remaining on the individual micro-mesh sieves during classification or sieving are shown in Figure 6. The sieves used were the $63\ \mu\text{m}$, $37\ \mu\text{m}$, and the $10\ \mu\text{m}$ mesh sizes. In the lower right is the fines collector. The figure shows that the aluminum and the activated carbon are physically separated

A



63 Micron Sieve

B



37 Micron Sieve

C



10 Micron Sieve

D



Fines Collector

Figure 6. Photographs of the Aluminum-Activated Carbon Mixtures Remaining on the Micron Sieve Screens After Sieving. (A) 63 μm sieve screen, (B) 37 μm , (C) 10 μm , (D) fines collector

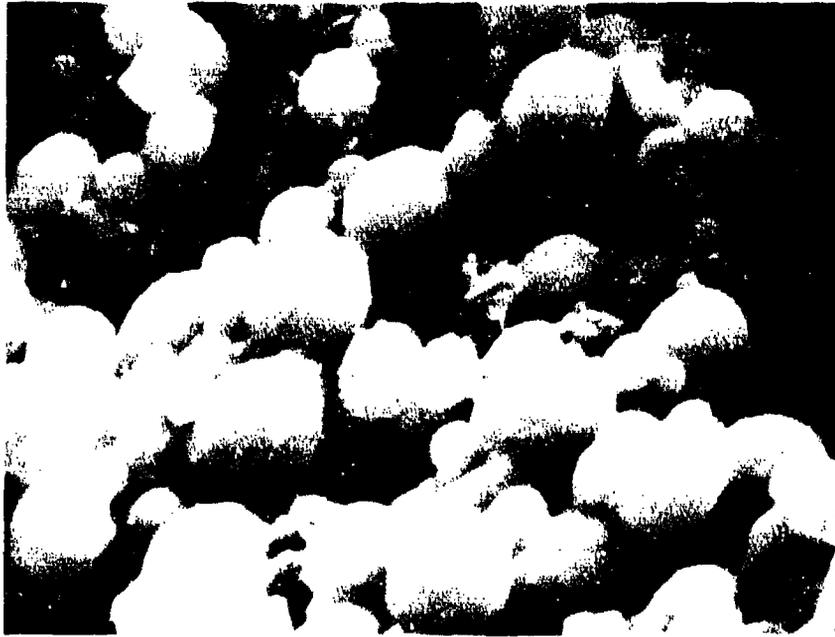
on the 63 μm sieve (Figure 6A). Partial separation of the aluminum spheres and the activated carbon has also occurred on the 37 μm sieve (Figure 6B). The solid on the 10 μm sieve (Figure 6C) is predominantly the activated carbon. The mixture in the fines collector (Figure 6D) is a finely divided composite of aluminum and activated carbon. Figure 6 shows that the aluminum remaining on the 63 μm and 37 μm sieves is probably the result of agglomeration of the aluminum particles before and during the sieving action.

The probable means by which the aluminum is deagglomerated is suggested in the scanning electron micrographs (SEM) shown in Figure 7. Small particles of the activated carbon are seen to cling to the surface of the aluminum sphere. The small carbon particles act as spacers which prevent the aluminum spheres from coming into large-area contact with one another, a circumstance under which molecular or van der Waals forces would be sufficiently strong to cause agglomeration. With small-area interparticle contact the effect of these forces would be considerably lessened. The activated carbon may also act as lubricant to facilitate movement of the aluminum spheres past one another. The result of these possible contributing factors is a free-flow aluminum mixture.

The results of sieve analyses of four types of J. T. Baker Chemical Co., activated carbon mixed with the aluminum are shown in Figure 8. All the aluminum/activated carbon mixtures in this and subsequent figures contained 20 percent activated carbon. In Figure 8 it can be seen that a range of deagglomeration effect was observed. Evidently it is not the composition (carbon), per se, that is instrumental in effecting deagglomeration, but other factors related to manufacture of the different types of activated carbon. The E-345 and E-344 types produce the greatest degree of deagglomeration, with 37 and 36 percent, respectively, of the mixtures passing through the 10 μm mesh sieve. Type E-346 produces an intermediate deagglomeration effect with around 30 percent of the mixture less than 10 μm in size. Type E-343 ranked quite low relative to the other carbons in that deagglomeration resulted only to the extent that around 10 percent of the mixture passed the 10 μm sieve. However, even this is an improvement over the untreated powder which has already been shown (Figure 5) to consist of essentially no particles smaller than 37 μm .

Figure 9 shows the particle size analyses of the activated carbon-aluminum mixtures prepared with several different types of activated carbon obtained from ICI United States Inc. (Darco). The best of these proved to be the material designated S-51. Approximately 42 percent of this aluminum/carbon mixture has a particle size less than 10 μm . The S-51 ranks second in performance to the activated carbon from Allied Chemical & Dye Corp. (Baker & Adamson, Code 1551) shown in Figure 5. The activated carbons, KB and G-60, are less promising but do give the aluminum mixtures a free flowing character and are clearly an improvement over the condition of the untreated aluminum powder.

A



B



Figure 7. Electron Photomicrographs Illustrating the Adherence of Small Carbon Particles to the Surfaces of the Aluminum Spheres. This attachment explains the deagglomeration effect of the activated carbon. (A) mag. 4750X. (B) mag. 9500X

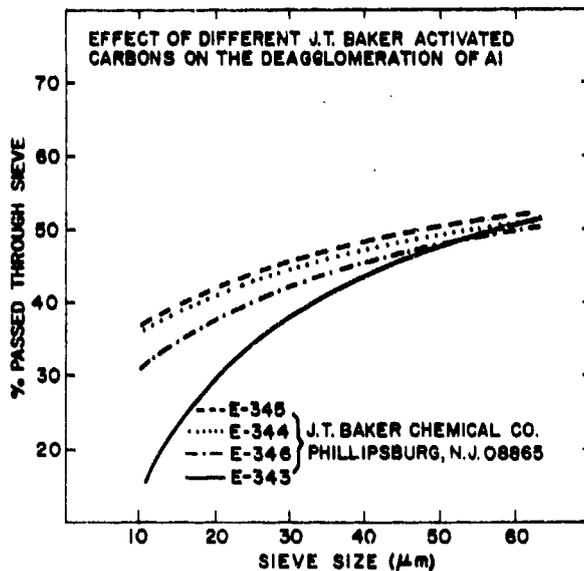


Figure 8. Size Analyses of the J. T. Baker Chemical Co., Activated Carbons-Aluminum Mixtures. All mixtures contained 20 percent activated carbon. Size analyses performed with an Allen-Bradley Sonic Sifter (Model L3P)

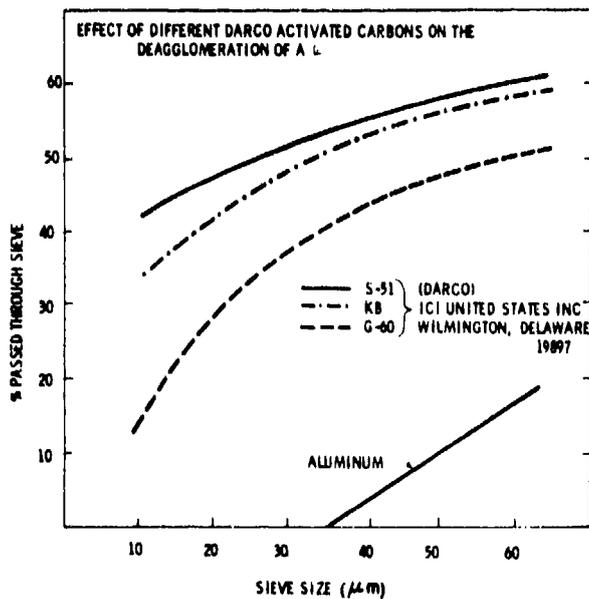
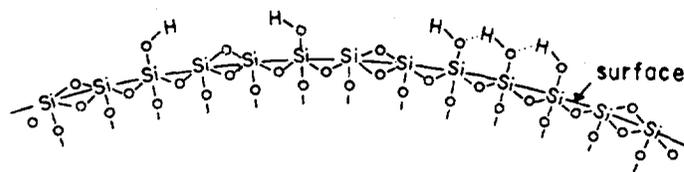


Figure 9. Size Analyses of the Darco Activated Carbons-Aluminum Mixtures. All mixtures contained 20 percent activated carbon. Size analyses performed with an Allen-Bradley Sonic Sifter (Model L3P)

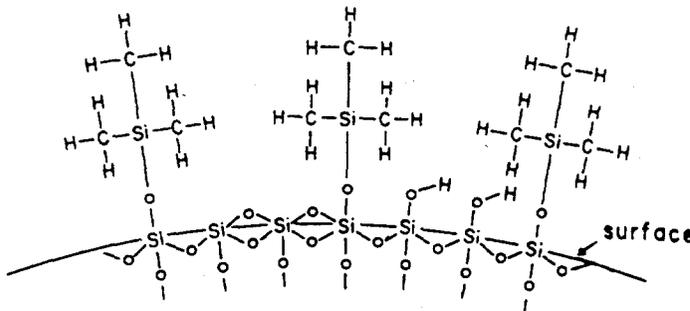
Addition of a Mallinckrodt Chemical Co. activated carbon designated type No. 4394 resulted in roughly the same degree of deagglomeration as the J. T. Baker Chemical Co., type E-346-carbon.

Another class of particulate additives investigated were the so-called fumed silicas formed by the hydrolysis of silicon tetrachloride vapor in an oxy-hydrogen

flame. Cab-O-Sil (Cabot Corp.) is fumed silicon dioxide and is used commercially for increasing the free-flow character of various granular and pelletized materials. A structural representation of the Cab-O-Sil surface is shown in the upper portion of Figure 10. This study showed that the addition of Cab-O-Sil to the Al powder greatly increased the dispersibility of the powder. Figure 11 shows the effect of different percentages of Cab-O-Sil on the deagglomeration of the aluminum powder. The sieve analyses indicate that the optimum deagglomeration effect of Cab-O-Sil is produced by additions in the 1 to 3 percent by weight range. Over this range, 53 to 55 percent of the aluminum/Cab-O-Sil mixtures were reduced to particles less than 10 μm in diameter. Actually, the best concentration may be closer to 1 percent because more of the remaining 47 percent of this mixture has been deagglomerated to particles between 63 μm and 20 μm in diameter than was observed in the 2 and 3 percent mixtures. Additions less than 0.5 and greater than 3 percent are less effective. With small additions the number of spacer particles is insufficient to isolate as many of the aluminum particles. This results in formation of fewer particles less than 10 μm in diameter and breakdown of gross aggregates but allows the forces of attraction to come into play in the bulk of the mixture to the extent that various degrees of aggregation to particle sizes in excess of 10 μm ensues.



CAB-O-SIL



TULLANOX 500

Figure 10. Molecular Structures of Cab-O-Sil and Tullnox-500

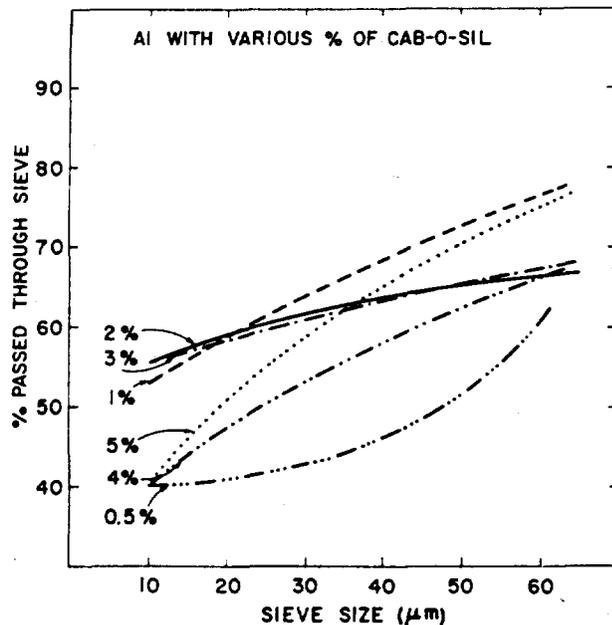


Figure 11. Size Analyses of Aluminum-Cab-O-Sil Mixtures With Varying Amounts of Cab-O-Sil. Size analysis performed with an Allen-Bradley Sonic Sifter (Model L3P)

With large additions it appears that there are sufficient Cab-O-Sil particles present to begin to interact with one another as well as with the aluminum spheres. Although breakdown of gross aggregates is achieved, there are, again, fewer particles in the less than 10 μm range. This behavior may be attributed to the fact that, during manufacture, hydroxyl groups become attached to some of the silicon atoms on the Cab-O-Sil particle surface. This makes the surface hydrophilic and capable of hydrogen bonding with suitable molecules in vapor, liquid or solid form; including the available oxygen sites on the surface of other Cab-O-Sil particles. It is quite likely that with excessive additions of Cab-O-Sil, the possibility of Cab-O-Sil to Cab-O-Sil particle contact is increased, thereby increasing the opportunity for hydrogen bonding to form an abundance of aggregates in excess of 10 μm in diameter. In any case, however, it must be re-emphasized that all of the Cab-O-Sil additions that were made resulted in improvement on the particle characteristics of the as-received aluminum powder, the sieve analysis of which is shown in Figure 5.

In order to circumvent the hydrogen bonding problem, a modified form of fumed silica, Tullanox-500, was also investigated. Tullanox-500 (Tulco, Inc.) is derived from fumed silicon dioxide where the hydrophilic hydroxyl groups on the surface are replaced with trimethylsiloxyl groups (see lower portion of Figure 10). Addition of Tullanox-500 to the aluminum powder increased its dispersibility. The effect of varying the percentages of Tullanox-500 on the dispersibility of the aluminum is shown in Figure 12. The optimum concentration for dispersing the aluminum powder below a size range of 10 μm is percent Tullanox-500. The amount

of aluminum powder in this size range is 78 percent. Addition of 3 percent Tullanox-500 is equally effective for dispersing Al powder below 10 μm but has the added advantage of giving the mixture a greater dispersibility below 63 μm .

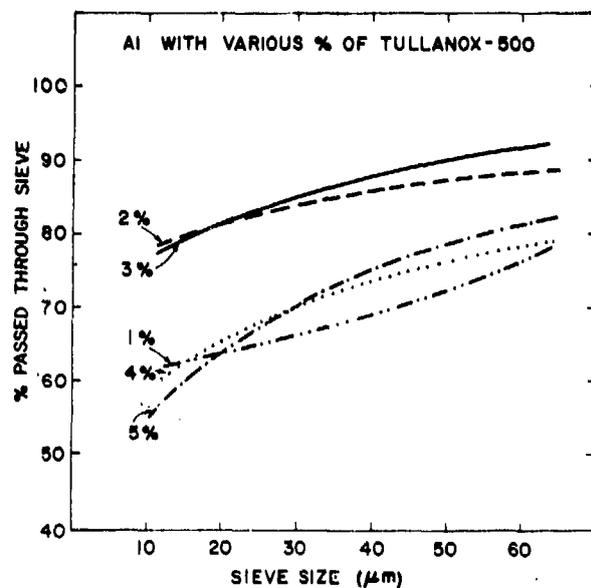


Figure 12. Size Analyses of Aluminum-Tullanox-500 Mixtures With Varying Amounts of Tullanox-500. Size analyses performed with an Allen-Bradley Sonic Sifter (Model L3P)

Comparison of the 2 percent mixtures of Tullanox-500 and Cab-O-Sil with aluminum is shown in Figure 13. Tullanox-500 is approximately 20 percent better than Cab-O-Sil. This difference can be attributed to the decrease in the availability of hydroxyl groups of the fumed silica for participation in hydrogen-bond formation. As explained above, the poor performance of large additions may be due to the presence of hydroxyl groups on the Cab-O-Sil surfaces. This effect inhibits the spacing properties of the fumed silica and promotes aggregation. Tullanox-500 does not possess these hydrogen bonding groups and therefore decreases agglomeration. The interspacing properties of Tullanox-500 remain intact.

A fourth material investigated as a possible deagglomerating agent was Micro-Cel (Johns-Manville, Inc.). This material is used commercially as a conditioning agent to provide improved flow characteristics and anti-caking properties for a wide variety of powdered and granular materials. Micro-Cel is a synthetic hydrous calcium silicate produced by the hydrothermal reaction of diatomaceous silica, hydrated lime and water. The ultimate particle size is stated to be as small as 0.02 to 0.07 μm . Thus, one may expect that it could function effectively as a spacer particle. Its free-flow promoting characteristics are based on a unique combination of properties: low bulk density, high absorptive capacity, varied particle size and

shape, and high surface area. This latter property is possessed in common with the activated carbons, Cab-O-Sil, and Tullanox-500; the additives previously discussed.

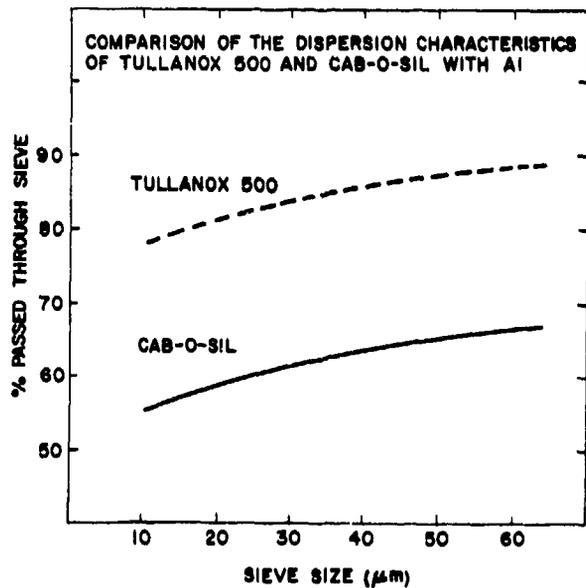


Figure 13. Comparison of the Deagglomeration Properties of Cab-O-Sil and Tullanox-500 on Aluminum Particles. The mixtures contained 2 percent of the spacer. Size analyses were performed with an Allen-Bradley Sonic Sifter (Model L3P)

Different percentages of the two types, designated Micro-Cel A and Micro-Cel C were added to the aluminum powder. Observation showed that addition of 2 percent of either type did not improve the dispersibility to any significant extent. However, addition of 20 percent of either type greatly improved dispersibility. The results are shown in Figure 14. The Micro-Cel A-aluminum mixture exhibited a particle size analysis with 61 percent of the particles below 10 μm . The Micro-Cel C mixture contained 53 percent particles below 10 μm . The difference in the dispersibility of the Al is possibly related to the particle size of the additive, where A is slightly larger than the C type.

The deagglomeration effect of Micro-Cel C is approximately the same as that of Cab-O-Sil, while Micro-Cel A is intermediate between Cab-O-Sil and Tullanox-500. Of all the additive materials investigated and listed in Table 1, Tullanox-500 showed the greatest deagglomeration effect.

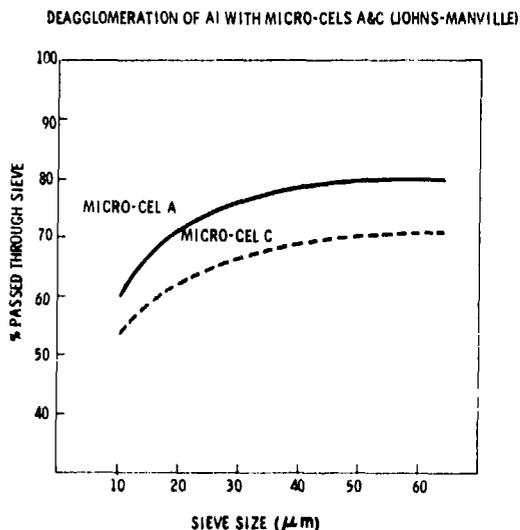


Figure 14. Size Analyses of Aluminum-Micro-Cels (Johns-Manville) Mixtures. Size analyses performed with an Allen-Bradley Sonic Sifter (Model L3P)

3.2 Coatings

This approach, as described under the Experimental Section, consisted of coating the aluminum particles using low molecular weight organic liquids or high molecular weight substances including polymers. The low molecular weight organics investigated were isopropyl alcohol, acetone, dimethylformamide, and dimethylsulfoxide (DMSO). Observations of the resulting powder specimens after treatment with the low molecular weight organics indicated that this approach did not warrant further study. The Al powder treated with isopropyl alcohol appeared to be slightly less agglomerated than the untreated powder.

The results obtained with the high molecular weight substances are shown in Table 2. The solvents used in each case are identified. The particles were coated by mixing the powder with the respective solutions or suspensions (teflon) followed by evaporation of the solvents. The free-flow character of the treated powders were then evaluated by visual observation.

Coatings of polyethylene glycol (m. w. 3000 to 3700), stearic acid in isopropanol, and colloidal teflon in suspension produced a slight improvement in deagglomeration of aluminum; with teflon having a slight edge on the others. However, even in this case the degree of improvement was inadequate. Figure 15 is a scanning electron micrograph (SEM) showing the extent and character of the teflon coating. The coating appears to be rather discontinuous and uneven, with some aluminum spheres more sparsely coated than others. Agglomerates of teflon particles also are evident. In the course of the teflon coating experiments, thin films containing the dispersed

powder were formed and were observed to possess an electrostatic charge which could prove to be troublesome.

Table 2. The Effect of Monomolecular Layers of Substrates on the Dispersibility of Aluminum Spheres

Coating	Solvent	Evaluation*
Acryloid-B72-100%	dimethylformamide	-
Polyethylene glycol (m. w. 3000-3700)	isopropanol	+
Polyethylene glycol (m. w. 600)	isopropanol	-
Stearic acid	isopropanol	+
Stearic acid	dioxane	-
Stearic acid	benzene	-
Styrene	n-heptane	-
Teflon DLX-6000	acetone	+
Teflon DLX-6000	triethylphosphate	+

*, - denotes no improvement; + slight improvement.

Experiments on photopolymerization of hexachloro-1,3-butadiene and tetrafluoroethylene (teflon monomer) deposited directly from the vapor on the aluminum spheres was carried out with the experimental apparatus arrangements shown in Figure 4.

A previous study by Wright⁴ showed that both hexachloro-1,3-butadiene and tetrafluoroethylene could be polymerized on aluminum slides by the action of ultraviolet light. The present study indicated that the hexachloro-1,3-butadiene was photopolymerized on the aluminum spheres. Visual examination showed that the particles had assumed a degree of stickiness, with the result that there was no improvement in the free-flow properties of the aluminum powder. Similarly, evidence that the tetrafluoroethylene had been polymerized was manifest by the presence of a deposit of waxy white teflon on the walls of the quartz reactors, as reported by Maylotte and Wright.⁵ In this case, too, little or no improvement in the free-flow properties of the aluminum powder was observed. Irradiated styrene-coated aluminum spheres exhibited slightly better free-flow character than the original.

4. Wright, A. N. (1967) Surface photopolymerization of vinyl and diene monomers, Nature, 215:953-955.

5. Maylotte, D. H. and Wright, A. N. (1974) Surface photopolymerization of tetrafluoroethylene, Faraday Discussions of the Chemical Society, No. 58, "Photo-effects in adsorbed species", pp 292-300.

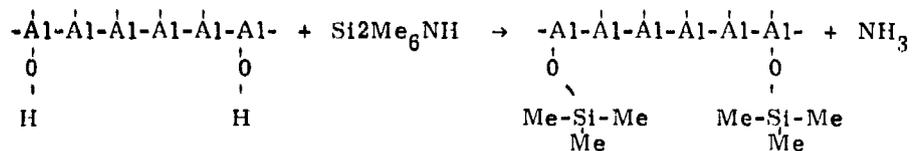


Figure 15. Electron Photomicrographs of Aluminum Spheres Coated With Teflon (mag. 9000X)

3.3 Surface Modification

This approach involved the chemical treatment of the surfaces of the aluminum spheres in order to reduce the attraction between them. The surfaces of the aluminum were modified by two methods: (1) Reaction of the Al surfaces with hexamethyldisilazane, and (2) Treatment of Al surfaces with water.

The first method consisted of reacting the hydroxyl groups of the aluminum surfaces with hexamethyldisilazane according to the following equation:



Bohemen et al⁶ showed that the reaction of the hydroxyl groups on firebrick with hexamethyldisilazane reduced its attraction for molecules. Therefore, reaction of the hydroxyl groups present on the Al surfaces with hexamethyldisilazane might be expected to give a free-flow character to the Al powder.

The above treatment on the Al surfaces gave a product whose dispersibility was slightly greater than the original. Shaking the mixture did produce a smoke, which indicated that a portion of the treatment was effective. Comparison of this method with the more promising methods indicate that its effectiveness is only marginal.

Treatment of aluminum with water using any one of the methods described in the Experimental Section yielded a superior free-flow product. The water treatment results in the formation of a continuous thin oxide film on the surface of the aluminum spheres--in contrast to the discontinuous flaky film which forms spontaneously on aluminum under ambient environmental conditions. Initially, the treated aerosol powder was spread in a thin layer in a large flat tray and air-dried. However, this was found to result in hard caking that necessitated moderate pounding and grinding in a mortar to break the product down into a free-flowing powder. This problem was caused by H₂O-bridging between particles which promoted the formation of oxide-bridging by the time the drying process was completed. To prevent this, the water was removed immediately following the reaction phase by successive acetone washes. The powder was then spread over the flat tray and air-dried for approximately one hour. The resultant product was a completely free-flowing powder requiring no further treatment. A particle size analysis of the material dried by both methods is shown in Figure 16. The figure shows that the water-treated aluminum washed with acetone gives an excellent dispersed aluminum powder with over 70 percent of the particles less than 10 μ m in diameter. On the other hand, the directly air-dried aluminum powder has less than 10 percent of the particles below 10 μ m. The reason for this is that the necessary grinding step is not completely effective in breaking down the aggregates formed by oxide bridging.

The improved dispersibility of the water-treated aluminum powder may be due to the continuous oxide film preventing metal-to-metal contact and the resultant attraction by cohesive forces that typically exist between metallic spheres. This is only partially accomplished in the case of aluminum particles with a naturally formed discontinuous oxide film, where a considerable number of particles may make metal-to-metal contact.

6. Bohemen, J., Langer, S. H., Perrett, R. H., and Purnell, J. M. (1960) A study of the adsorptive properties of firebrick in relation to its use as a solid support in gas-liquid chromatography, J. Chem. Soc., pp 2444-2451.

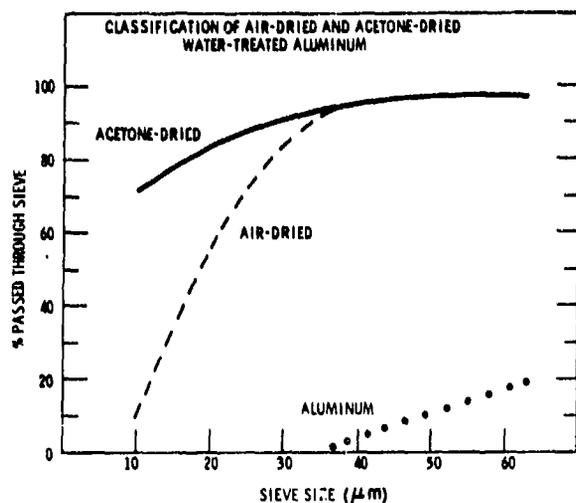


Figure 16. Comparison of Size Analyses of the Water-Treated Aluminum Dried Directly and Dried After Acetone Washes. Size analyses performed with an Allen-Bradley Sonic Sifter (Model L3P)

A contribution may also be due to the possibility that because the natural film formed by adsorption of oxygen from the atmosphere is very thin--of the order of several \AA in thickness--it may be inadequate for screening the forces of attraction. Also, with a very thin oxide film, the aluminum spheres can still deform at the interparticle contact to form a large-area contact resulting in increased adhesion and subsequent agglomeration. Ranade⁷ points out that the increased hardness or rigidity imparted to the aluminum spheres by the 50 to 100 \AA -thick Al_2O_3 film formed by the controlled reaction method would limit this deformation, thereby promoting a decrease in interparticle adhesion and improvement in dispersibility.

4. SUMMARY AND CONCLUSION

An in-house effort was conducted in support of an MIT Lincoln Laboratory (SAMSO/ABRES) program to develop a method for deagglomerating an aluminum powder in order to realize its optimum IR signature. Essentially, the problem was to overcome the forces of attraction between solid particles which are sufficiently strong to cause agglomeration or clustering when the particles are in the micron size range.

7. Ranade, M. B., Private Communication.

Observations of the Al powder behavior in the course of sounding rocket tests by MIT Lincoln Laboratory indicated that this might be accomplished by shielding or separating the particles from one another. Accordingly, three approaches were investigated,

- (1) The use of additive particulate material to act as spacer-particles,
- (2) Coating or encapsulation of the aerosol particles with polymers and other substances, and
- (3) Modification of the surface of the aerosol particles by chemical means.

The treated Al powder was evaluated by visual observation of bulk-shear and settling characteristics following agitation and by sieve analysis or particle classification. Samples were then transmitted to Lincoln Laboratory for further evaluation by zero-G and sounding rocket dispersal testing.

Both the spacer-particle and surface modification approaches were found to be very effective in converting the highly agglomerated aluminum to a free-flowing condition. Of the various coatings investigated, only teflon showed promise. Dispersibility of the powder was marginal in comparison to the spacer and surface modification approaches. However, further experimentation with teflon suspensions could prove to be of value.

As determined by visual examination and sieve analysis based on the proportion of aerosol/admixture less than 10 μm in diameter, the following additives, ranked in order of effectiveness, were found to be potentially useful deagglomerating agents,

- (1) 2 percent Tulco Tullanox-500 (trimethylsiloxy-modified fumed silica),
- (2) 20 percent Johns-Manville Micro-Cel (calcium silicate),
- (3) 20 percent Baker & Adamson, Code 1551, activated carbon,
- (4) 2 percent Cabot Cab-O-Sil (fumed silica)
- (5) 20 percent ICI United States Darco S-51 activated carbon, and
- (6) 20 percent J. T. Baker E-345 and E-344 activated carbon.

Surface modification by controlled reaction with heated water produced outstanding deagglomeration when combined with acetone drying which prevents oxide-bridging.

Sieve analyses of the resulting aluminum powder from the favorable treatments are shown in Figure 17. The untreated aluminum is shown for comparison.

At this writing, aerosol with added Baker & Adamson activated carbon has been reported as performing better than any treated aerosol previously tested under zero-G conditions. Emphasis on the design of hardware to accommodate the agglomeration problem has delayed advanced testing of the other promising aerosol modifications.

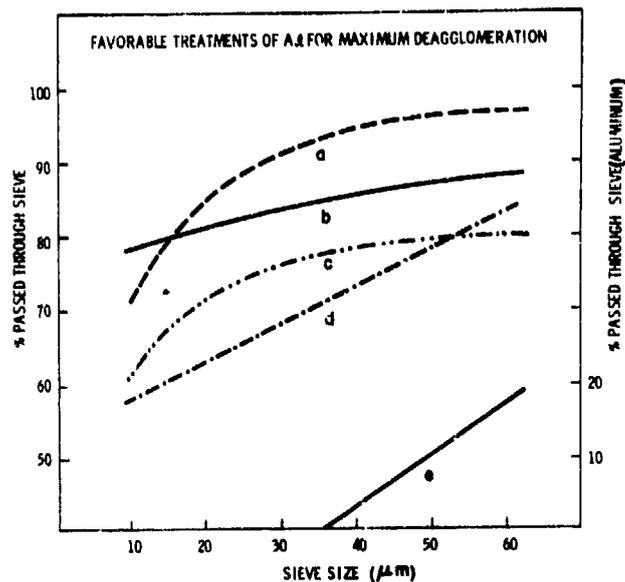


Figure 17. Size Analyses of the Aluminum Mixtures Which Display Improved Optimum Dispersibility. (a) Water treated-acetone dried. (b) Addition of 2 percent Tullanox. (c) Addition of 20 percent Micro-Cel A. (d) Addition of 20 percent activated carbon (Baker & Adamson). (e) Untreated aluminum. The right ordinate corresponds to the untreated aluminum. Size analyses performed with an Allen-Bradley Sonic Sifter (Model L3P)

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7. Ranade, M. B., Private Communication.

