for $y \geq y_c$, $\rho = \rho_e$ and $u = u_e$. It is assumed also that $\partial(\rho e u_e)/\partial y = 0$ for $y \geq y_c$.

Continuity is applied to yield the mass balance within the control surface,

$$\int_0^{y_c} (\rho u)_2 dy = \int_0^{y_c} (\rho u)_1 dy + \int_{x_1}^{x_2} (\rho_w v_w - \rho_e v_e) dx \quad (1)$$

and the usual definition of displacement thickness δ^* is introduced through the equation

$$\begin{aligned} \int_0^{y_c} (\rho u) dy &= \rho_e u_e \left[y_c - \int_0^{y_c} \left(1 - \frac{\rho u}{\rho_e u_e}\right) dy \right] \\ &= \rho_e u_e [y_c - \delta^*] \end{aligned} \quad (2)$$

When Eq. (2) is substituted into Eq. (1) and the limit as $(x_2 - x_1) \rightarrow 0$ is taken, the result is

$$\rho_e v_e\big|_{y=y_c} = \rho_e u_e (d\delta^*/dx) + \rho_w v_w - (y_c - \delta^*)[d(\rho_e u_e)/dx] \quad (3)$$

The first two terms on the right-hand side of Eq. (3) represent the vertical component of mass flow induced by the boundary layer. The last term on the right side [i.e., $-(y_c - \delta^*)d(\rho_e u_e)/dx$] is the vertical component of mass flow which would exist at a normal distance $(y_c - \delta^*)$ from a solid body for the case of inviscid flow with a surface axial mass flow gradient $\partial(\rho_e u_e)/\partial x$ and $\partial(\rho_e u_e)/\partial y = 0$.† This can be seen from the continuity equation of the inviscid flow,

$$\partial(\rho_e v_e)/\partial y = -\partial(\rho_e u_e)/\partial x \quad (4)$$

which leads to

$$\rho_e v_e\big|_{y=y_c} = \rho_e v_e\big|_{y=\delta^*} - \int_{\delta^*}^{y_c} \frac{\partial}{\partial x} (\rho_e u_e) dy \quad (5)$$

Now for $\partial(\rho_e u_e)/\partial x$ independent of y, Eq. (5) becomes

$$\rho_e v_e\big|_{y=y_c} = \rho_e v_e\big|_{y=\delta^*} - (y_c - \delta^*)[d(\rho_e u_e)/dx] \quad (6)$$

Thus, this additional vertical-mass-flow term is associated with the inviscid flow and must be neglected when computing the boundary layer displacement effect. (Note also that this term varies linearly with y_c and therefore is not defined uniquely.)

Neglecting the last term on the right-hand side of Eq. (3) and dividing by $\rho_e u_e$ gives the incremental flow angle induced by the boundary layer:

$$\frac{v_e}{u_e} \cong \theta_w \cong \frac{d\delta^*}{dx} + \frac{\rho_w v_w}{\rho_e u_e} \quad (7)$$

The effective boundary layer displacement thickness is

$$\int_0^x \theta_w dx \cong \Delta^* = \delta^* + \int_0^x \frac{\rho_w v_w}{\rho_e u_e} dx \quad (8)$$

The point emphasized is that the term δ^* is calculated from the boundary layer density and velocity profiles under the influence of blowing as obtained by the appropriate boundary layer solution, but the displacement effect on the external flow should include the additional term involving injected mass flow. It is believed that the necessity for including this additional mass-flow term in the calculation of interaction effects on ablating bodies generally has not been recognized.

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† This interpretation of Eq. (3) was pointed out to the author by H. Mirels of the Laboratories Division, Aerospace Corporation.

Particle Size Analysis of Ammonium Perchlorate by Liquid Sedimentation

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A method is described for obtaining particle size distributions in ammonium perchlorate and other finely divided materials from 400-μ diam to 1 μ and below. The method offers advantages including rapid operation and moderate equipment costs. Validity and accuracy of the method are found to be satisfactory for use in studies of particle size effects in solid propellant combustion.

Introduction

AMMONIUM perchlorate currently is used by many manufacturers as an oxidizer in composite solid propellants. In most cases this crystalline material is used partly or entirely in a finely ground condition. It long has been recognized that the average size and size distribution of the perchlorate particles are factors that influence the combustion behavior of such propellants. An experimental program has been completed recently at Princeton wherein the effects of these factors on burning rates were determined for various propellant compositions.[1, 2] At the outset of this program, it was necessary to obtain an instrument for measuring particle size distribution.

Measurement of fine particles is a complex subject, and methods that presently are known are numerous and varied.[3] However, for particles in the so-called subsieve range, that is, particles less than 50 μ in diameter, methods most often used for measuring size distribution are based on the movement of particles through a fluid. This process lends itself to rapid and repeated analysis more than any other.§ Instruments vary widely in nature, but the basic principle of operation is the same. The velocity with which a particle moves through a fluid is dependent upon the force acting upon the particle, the fluid viscosity, and the particle size and shape (for low Reynolds numbers). The effect of particle shape generally is avoided by assigning to each particle a diameter equal to that of a sphere of equal density which moves through the fluid with the same velocity. For nearly spherical particles, this device is satisfactory. Many instruments allow particles to fall (or rise) under the influence of gravity. This is called the sedimentation method. Others increase the force field by centrifugal action. In a constant force field, particle velocity is very sensitive to size, particularly in the Stokes regime, where velocity is proportional to the square of the particle diameter. Thus, instruments based on this principle are capable of indicating particle diameter with great accuracy.

In measurement of ammonium perchlorate particles, a number of special problems are encountered. Finely ground

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§ Rapid methods based on other principles do exist for measuring a *mean* particle size.

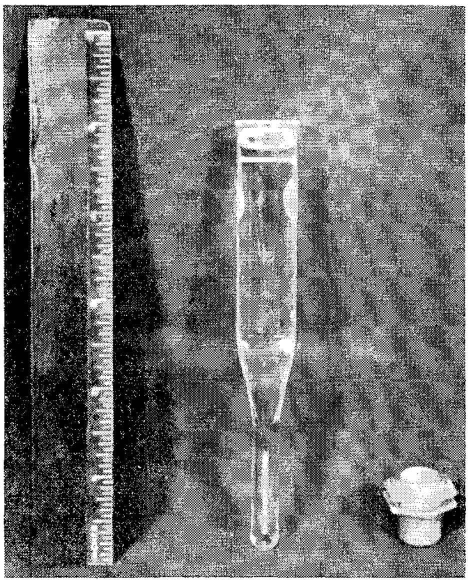

Fig. 1 Centrifuge tube and feeding chamber for particle size analysis

perchlorate tends to agglomerate severely. Consequently, any instrument for size measurement must incorporate a means for complete dispersion of the particles to avoid erroneous results. In addition, ammonium perchlorate is water-soluble and hygroscopic, and in the choice of sedimentation fluid, the need for an anhydrous system must be kept in mind.

Probably the most common method of size analysis used in the propellant industry is air sedimentation. A widely used instrument based on air sedimentation is the Micromerograph manufactured by the Sharples Corporation, Philadelphia, Pa.

Several methods of particle size analysis were investigated at the outset of the program of research on particle size effects at Princeton. These included air sedimentation, liquid sedimentation, light scattering, and a novel method based on the variation of electrical resistance through a liquid-filled orifice as particles are drawn through it.[‖] The method that was selected for use in this laboratory is a liquid sedimentation method employing both gravity and centrifugal settling, developed by Whitby of the University of Minnesota.[4] It had been used previously for many materials such as dusts, minerals, and foodstuffs but had not been adapted for use with ammonium perchlorate. The apparatus employed was manufactured by the Mine Safety Appliance Company, Pittsburgh, Pa. The method was selected primarily because of the relatively low cost of equipment, but early testing indicated that the method offered accuracy and rapid operation as well.

Description of Method

Particle size analysis is carried out in a liquid-filled glass centrifuge tube that is shown in Fig. 1. The tube is approximately 10 cm in length, and the upper section has a bore of approximately $1\frac{1}{2}$ cm. In the lower section of the tube, the bore converges to a precision bore capillary section that is 2 to 3 cm long. Tubes can be obtained with capillary bore diameters of $\frac{1}{2}$, $\frac{3}{4}$, or 1 mm.

The operating procedure is indicated in Fig. 2, which was reproduced from Ref. 5. A centrifuge tube is filled with the sedimentation liquid and placed in a projector that displays a magnified image of the capillary portion of the tube. A sample of the particles to be measured is introduced into a "feeding liquid" (which is of somewhat lower density than the sedimentation liquid), and a well-dispersed dilute suspension is formed by vigorous agitation.[#] Approximately 1 ml of the suspension is transferred to the centrifuge tube by means of a small feeding chamber. The suspension is floated on top of the sedimentation liquid, and the particles fall under the influence of gravity. This transfer is accomplished quickly so that the particles still are dispersed when they reach the centrifuge tube. When the suspension is released into the tube, a clock is started. As the particles reach the bottom of the capillary, a sediment column is formed, and the height of this column in the capillary is recorded as a function of time. The column height generally is measured at predetermined times that correspond to conveniently spaced intervals of particle diameter.

As the particles reaching the tube bottom become smaller, the rate of accumulation becomes slower. When this occurs, the tube is transferred to a slow-speed centrifuge for a brief period of time, after which the sediment column height is measured again. This step is repeated for longer times and at higher speeds until the column height remains constant. This indicates that all particles have been centrifuged out. At the end of the procedure, the total column height is noted. A typical schedule of operation is shown in Table 1. In this schedule, particles are allowed to settle under gravity for approximately 4 min, at which time all particles larger than 25 μ have reached the bottom of the tube. At this point, a series of centrifuge runs is started. Allowing for starting and stopping times, this portion of the schedule can be carried to 3-μ particles in about 10 min. Additional centrifuging for 20 min will cause particles down to 1-μ-diam to settle out. These times are typical for most measurements

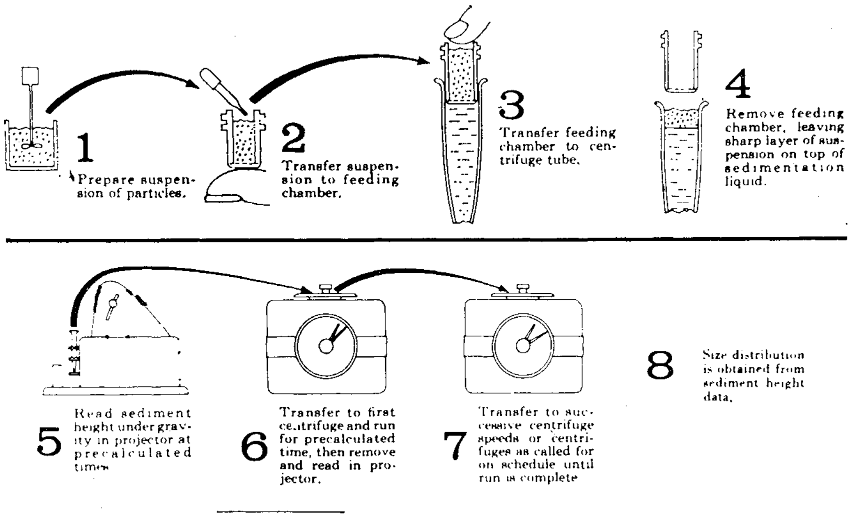

Fig. 2 Basic steps in particle analysis with MSA particle size analyzer

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[‖] This device is manufactured by Coulter Electronics Inc., Chicago, Ill.

[#] For this purpose, a Brookfield counter-rotating stirrer, agitating 100 ml of liquid in a 250-ml beaker, is satisfactory.

Table 1 Schedule of operation for particle size analysis of ammonium perchlorate in chlorobenzene at 75°F

Gravity sedimentation		
Particle diam, μ	Settling time, sec	
100	16	
80	26	
60	46	
50	66	
45	81	
40	103	
35	135	
30	183	
25	264	
Centrifugal sedimentation		
Particle diam, μ	Centrifuging time, sec	Speed, rpm
20	13	300
15	35	300
10	30	600
7.5	44	600
5	39	1200
3	110	1200
1	1297	1200

with this equipment. The method of calculation of the operating schedule is given in Refs. 4 and 5. The time for a particle to reach the bottom of the tube by gravity sedimentation is calculated using the following formula:

$$t = [18\mu_0 l/g(\rho - \rho_0)d^2]$$

wherein μ_0 and ρ_0 are the absolute viscosity and density of the sedimentation liquid, l is the tube length, g the gravitational acceleration, and ρ and d the density and diameter of the particle. This relation is based on Stokes' law for spheres, and, thus, the diameters obtained are Stokes' equivalent diameters.

When the measurements have been completed, a particle size distribution is obtained simply by dividing each column height measurement by the total height. This gives the percentage of the column made up of particles larger than that diameter corresponding to the time at which the measurement was taken. This is also the percentage by volume of particles above this diameter. If the bulk density of the particles in the column is assumed to be constant with particle size, this value also is equal to the percentage by weight. This assumption has been found to be valid in most cases. Thus, a weight distribution of particle sizes is obtained easily from the data taken.

As indicated in the forementioned procedure, two liquids are necessary for the operation: a feeding liquid in which the particles are dispersed, and a sedimentation liquid in which the test is performed. The sedimentation liquid is selected on the basis of viscosity and density that determine the particle velocity and, therefore, the measurement interval. The combination of viscosity and density required depends upon the size range and density of the particles to be measured. The feeding liquid must be miscible with the sedimentation liquid, similar in viscosity, and at least 10% less dense. All these requirements must be met to provide proper feeding of the particles into the sedimentation liquid. In addition to these requirements, both liquids must be chemically inert to the particles and must not dissolve them. Finally, both liquids must be able to support a dispersion of the particles without interaction between the particles (flocculation) or between the particles and the container walls (sticking). Various wetting agents are found to aid in meeting this requirement.

Several liquids were investigated for use with ammonium perchlorate. Two sets of liquids are used routinely for different particle size ranges. A low viscosity set, for particles in the range 1 to 100 μ, consists of chemically pure chlorobenzene as the sedimentation liquid and chemically pure benzene as the feeding liquid. A small amount of wetting agent is necessary with each of these.** A higher viscosity pair of liquids, for larger particles, consists of diethyl phthalate as the sedimentation liquid and di-n-butyl-sebacate as the feeding liquid. Wetting agents are not required with these. Particles as large as 400 μ have been measured with the more viscous fluids, but special precautions must be taken, and accuracy is reduced somewhat.

Validity of Method

The most serious question affecting the validity of the method stems from the assumption of equivalence of volume fraction (column height fraction) to weight fraction. This assumption was shown to be valid in the following way. A sample of ground ammonium perchlorate was dispersed in benzene, and samples of the suspension were inserted into six different centrifuge tubes. Sedimentation was allowed to proceed according to the appropriate schedule until all particles greater than a size selected for each tube had settled (using the appropriate centrifuges where called for). The suspension above the column then was removed and the final column height noted. The sedimentation liquid was driven off by oven drying, and the tubes were weighed on an analytical balance. The weight of the column of oxidizer in each tube was determined by difference, and the weight per unit of column height in each tube was computed. The value of weight per unit height was the same for all six tubes within ±2%. Particle sizes ranged from 200 to 60 μ in the first tube and 200 to 1 μ in the sixth, with other tubes ranging between these extremes. Actual bulk density of the sediment column was found to be similar to that of narrow size fractions of ground perchlorate, which is 1.0 g/ml. When unground perchlorate was analyzed, the bulk density of the sediment column was found to be 1.3 g/ml. This value also is obtained with sieved fractions of coarse material. The difference is attributed to a difference in particle shape.

Thus, the assumption of constant bulk density is valid as long as the material to be tested is entirely ground or unground. It probably is not desirable to perform particle size measurements on mixtures of ground and unground material because of the possible error that might arise as a result of the bulk density difference.

Other aspects of the method which conceivably could lead to errors have been checked, and no serious discrepancies have been discovered. These include checks of uniformity of capillary bore diameter, linearity of column height scale on the projector, and the compacting of the sediment column due to centrifuging.

To check the accuracy of the results of the method, arrangements were made for the analysis of several samples of ammonium perchlorate (containing anti-caking agent) by air sedimentation in the Micromerograph at two other laboratories.†† The same samples then were analyzed at Princeton by liquid sedimentation. Results of the analyses of two samples are shown in Fig. 3. The results for the fine sample agree fairly closely. However, the upper portions of the curves suggest failure of the Micromerograph to achieve complete deagglomeration. Microscopic examination of this sample revealed no particles larger than 50 μ in diameter. Agreement among the results for the coarse sample

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** Wetting agent used is Twitchell Base 8240 (Emery Industries) at the rate of one drop per 25 ml. However, several other agents, including lecithin, have been found to be equally effective.

†† The two cooperating laboratories were engaged in routine quality-control particle size analysis of ammonium perchlorate in conjunction with the manufacture of composite solid propellants. For this assistance, the authors are indebted to Henry Shuey of the Redstone Research Division, Rohm and Haas Company, Huntsville, Ala., and to Gordon Leader of the Elkton Division, Thiokol Chemical Corporation, Elkton, Md.

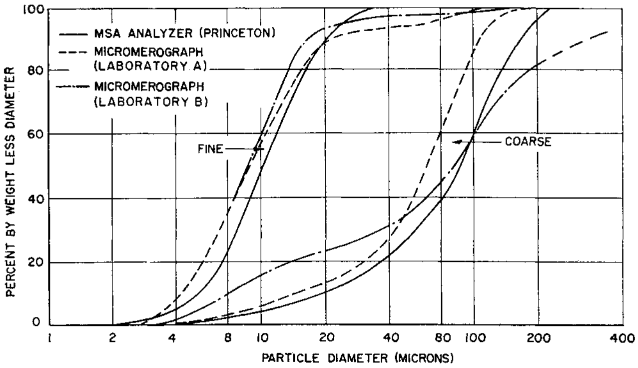

Fig. 3 Comparative particle size analyses; ground ammonium perchlorate, two grinds

is less satisfactory. However, disagreement between the two methods is not surprising since, in this size range, particles settling in air are far out of the Stokes regime, and transition from one regime to another is difficult to predict for nonspherical particles. Thus, results may be expected to vary from those from liquid sedimentation (where the behavior is entirely within the Stokes regime). The authors have no explanation to offer for the disagreement between the two Micromerograph results. (An interesting discussion of reproducibility of analyses using the Micromerograph can be found in Ref. 6.)

Liquid sedimentation analysis by the Whitby method has proved to be both a rapid and accurate method of particle size measurement for ammonium perchlorate. The technique appears superior in speed, precision, and first cost to the air sedimentation method commonly used in the solid propellant industry, but greater operational skill and judgment are required in its use.

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On Mass Transfer Effectiveness

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Nomenclature

ϵ = error
R = effectiveness, $(T_w - T_c)/(T_{aw0} - T_c)$
h = heat transfer coefficient
F_c = injection ratio, $(\rho v C_p)_c/(\rho u C_p)_\infty$
ρ = density
v,u = velocities
C_p = specific heat at constant pressure
St = Stanton number, $h/(\rho u C_p)_\infty$
T = temperature

Subscripts

0 = zero injection condition
c = coolant
w = wall
aw = adiabatic wall

In a recent note the usefulness of the "effectiveness" R as a correlating parameter for data on the mass transfer cooling of turbulent boundary layers was questioned.[1] This quantity was suggested originally, though not so-called, by Friedman,[2] in a study of low-speed flow. The authors of this paper had remarkable success with it in correlating carefully taken data at Mach numbers 2 and 3.2 in flat plate flow when the coolant gas was nitrogen and the freestream gas was air.[3] When, within experimental error, later sets of data at Mach numbers 3.2 and 6.7 (Refs. 4 and 5, respectively) for a wide variety of coolant gases were found to correlate well with the previous data, the effectiveness as a "universal" parameter was proposed.[4] This must be regarded, of course, as a postulate that will be subject to the evaluation of future research.

It was recognized that the effectiveness, as previously defined,[6] has a singularity at $T_c = T_{aw0}$. Under these conditions the denominator is zero, whereas the numerator is different from zero unless for that particular case $T_c = T_w$. From the energy balance,

$$h(T_w - T_{aw}) = (C_p \rho v)_c (T_w - T_c) \tag{1}$$

it may be seen that this exception occurs only if $T_w = T_{aw}$, which amounts to the condition $T_{aw} = T_{aw0}$, i.e., that coolant injection does not affect the recovery factor. This special case thus far has been measured only for transpiration (air into air) at zero Mach number. Thus, the existence of a singularity in R may be expected in general as T_w is varied through values in the vicinity of T_{aw0}, but in practice $T_w \ll T_{aw0}$. This singularity would not exist if one adopted a slightly different "effectiveness," namely, $R' = (T_w - T_c)/(T_{aw} - T_c)$, and in practice $R = R'$ because $|T_{aw} - T_{aw0}|/(T_{aw0} - T_c)$ is very small.

After some manipulation, the effectiveness may be expressed as

$$R = [1 + (F_c/St)(T_w/T_{aw0} - 1)/(T_w/T_{aw0} - T_{aw}/T_{aw0})]^{-1} \tag{2}$$

For this discussion, regard St/St_0 and T_{aw}/T_{aw0} as fixed when F_c/St_0 is given, and, hence, R depends only upon T_w/T_{aw0}. T_w/T_{aw0} may vary from zero to infinity, but in practice its value generally will be less than 10^{-1}. In conducting experiments with nitrogen injection, data were obtained which yielded the two branches of the hyperbola shown for two typical conditions in Fig. 1.

The important deviation of R due to the singularity is seen to be confined to the range $0.9 < T_w/T_{aw0} < 1.1$, approximately. Furthermore, under the assumption that St/St_0 is determined uniquely by F_c/St_0, data at any one value of T_w/T_{aw0} are sufficient to determine both branches of the curve in its entirety. The assumption implies that heat transfer is proportional to $T_w - T_{aw}$, for $0 \leq T_w \leq \infty$, or, in other words, that a plot of $T_w - T_c$ vs T_w is linear, passing through zero at $T_w = T_{aw}$. This assumption may be incorrect for extremely hot or cold walls, but it is known to be correct for moderate temperature differences.

With attention confined to the neighborhood of the singularity, it is possible to insist that the forementioned assumption is valid at $T_w/T_{aw0} = 0.9$ and 1.1. Therefore, measurements made at $T_w/T_{aw0} = 1.1$ should be valid at $T_w/T_{aw0} =$

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