

The sizing of some powder and liquid sprays from pressurized packs by air sedimentation

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The construction and testing of an apparatus suitable for the size analysis of certain pressurized sprays by air sedimentation is described. Talc spray size was related to the size of the talc used to prepare the pressurized pack. For other powders (UFI and neomycin sulphate) the sprays were much larger than the powder used to prepare the pack. The use of propellents of higher vapour pressures, higher pack temperatures and the addition of 0.5% sorbitan monolaurate resulted in smaller talc sprays. Talc spray size was increased by the addition of 0.5% isopropyl myristate. Increasing the viscosity of the liquid product and increasing the concentration of propellant gave a reduction in liquid spray size; for both liquid and talc sprays, smaller sprays resulted from the use of a valve housing with a vapour tap.

The size analysis of sprays from pressurized packs by microscopy (C.S.M.A., *Aerosol Guide*, 1966; Lefebvre & Tregan, 1964) is tedious and time-consuming and the results may be unreliable because of the necessity for calibration, the likelihood of size changes taking place between collection and sizing, and because the sampling is often biased. The use of the Cascade Impactor can shorten the analysis (Polli, Grim & others, 1969) but an initial calibration of the apparatus by microscopy is still required and drops with diameters greater than 50 μm settle out of the spray before being impacted on the first slide.

A sedimentation column of height 6 m and diameter 0.74 m with an automatically recording balance at the bottom of the column was used to size non-volatile liquid and solidified liquid fuel drops of 5-250 μm diameter (Tanasawa & Hiroyasu, 1962). Such a tall column was necessary for adequate separation of the different sized drops. Further, the time taken for a drop to reach its terminal sedimentation velocity was small compared to its overall fall time so that it could be assumed that each drop travelled down the whole of the column at its terminal velocity.

MATERIALS AND METHODS

Apparatus

A sedimentation column (Fig. 1), 27.5 feet high and 27 inches in diameter, was made from 3/16 inch "Darvic" PVC sheeting. An earthed coating of powdered graphite applied to the inner surface of the column kept the PVC uncharged. The column was erected against the outside wall of the building and the top and bottom entrance boxes projected into the first floor and basement of the building respectively.

Thermistors (S.T.C., type F.S.) were inserted through the column wall at several points for the measurement of air temperatures.

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An automatic continuous recording balance (Fig. 1) recorded the weight of sedimented particles, the position of a sliding weight on the balance pointer being set to give a linear balance response over the range 0–150 mg. The balance scale pan with a diameter just less than the internal diameter of the column, was made of "Propafilm O" gauge 50/515 supported by a light-weight frame. Movements of the balance beam were recorded by reflection of a light beam from a mirror on the balance beam onto photographic recording paper on the kymograph. A time marker was obtained on the kymograph recording by interrupting, at 1 min intervals, the current to the light source. Balance oscillations were damped by the small vane at the end of the balance pointer moving in a dash-pot containing liquid paraffin B.P.

Even after the column had been sealed for several hours there were air currents in the region of the balance. Insulating or heating the whole or part of the column, or both, did not reduce these movements. The use of more efficient damping and the attachment of springs to the balance beam reduced balance movements but also greatly reduced the sensitivity of the balance. The air movements were reduced by

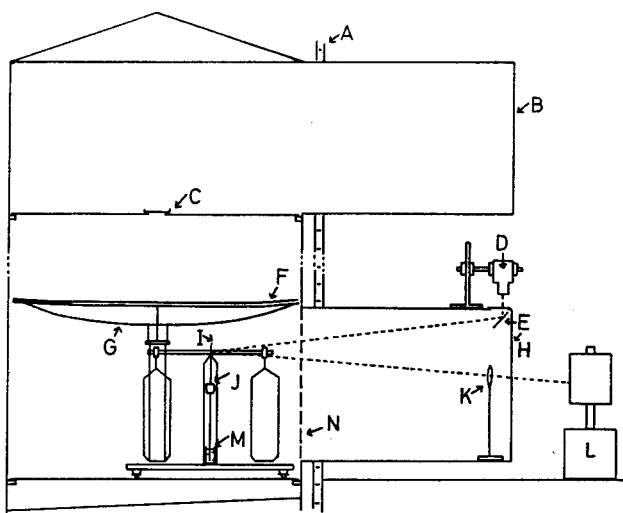


FIG. 1. Sedimentation column and balance. A, wall of building; B, top entrance box; C, shutterplate; D, lamp; E, front-silvered plane mirror; F, scale pan; G, scale pan supports; H, bottom entrance box; I, front-silvered concave mirror; J, sliding weight; K, convex lens; L, kymograph; M, dash-pot containing damping liquid; N, position of baffle.

introducing carbon dioxide through the bottom of the column at flow rates up to 1.8 litre/min; the performance of the balance was unaffected. Higher flow rates increased air movements. The introduction of carbon dioxide at 1.8 litre/min for 60 min abolished balance movements and even after the gas flow was stopped they remained at this low level for several hours. Determination of the carbon dioxide content of the air in the column using a CO_2/O_2 electrode (Norman, Ledsoe & Linden, 1965) showed that the carbon dioxide concentration fell off rapidly with height above the floor of the column. The results are shown in Table 1. Because of the difficulty of maintaining stability for very long settling times particles having diameters less than $5 \mu\text{m}$ were not sized.

The introduction of a sample for analysis was controlled by a shutterplate mounted over the sampling hole in the centre of the platform at the top of the column. So

Table 1. *Percentage of carbon dioxide in the gas removed from the column before, during and after the introduction of carbon dioxide gas at the rate of 1.8 litre/min.*

Time (min) after the start of input of carbon dioxide	Position up the column		
	Between floor of column and thermistor 1	Level with thermistor 1	Level with thermistor 2
0	0.2	0.1	0.1
30	5.6	0.3	0.2
60	17.0	0.9	0.3
90	26.6	3.4	0.4
After 90 min carbon dioxide input stopped.			
120	21.9	3.3	
150	16.2	3.3	
180	12.9	2.8	
210	11.5	2.3	

Thermistor 1 was level with the balance scale pan; thermistor 2 was 5.5 ft higher up the column.

that the spluttering of the valve on opening and closing was not included in the sample analysed, the shutterplate movements were controlled electrically to give the following sequence: depression of the actuator button, opening of the shutterplate and sample introduction, closing of the shutterplate, release of actuator button. Any spray released before opening and after closing of the shutterplate was collected on the shutterplate. The sampling time, 1–2 s for the introduction of 100 mg of spray, was marked on the kymograph recording.

Each pressurized pack was kept in a temperature-controlled water bath for a standard time before operation and sampling. During sampling the pack was held horizontally with the orifice of the actuator button above the centre of the shutterplate, the open end of the dip tube being covered by the liquid in the pack. In accordance with the manufacturer's instructions the urea formic iodide (UFI) packs were held at an angle of 45°, with the orifice of the actuator button 12.5 inches from the centre of the shutterplate. The talc, neomycin sulphate and liquid product packs were held with their actuator buttons 3.5 inches above the shutterplate. Evaporation of propellant appeared to be complete from the spray thus introduced into the column. As the spray sample had to remain unchanged during its sedimentation and collection, the investigation was confined to powders and non-volatile liquid products.

Preparation of pressurized packs

With the exception of the UFI packs all packs were assembled from components in the Precision Valve Kit (Metal Box Company).^{*} Except for the actuator button, which was shaved down so that the orifice no longer lay in a recess, all were used exactly as supplied. The UFI packs used were either the standard commercially available pack or a modification specially prepared by the manufacturer. The other packs were prepared in the laboratory using an ambient temperature technique.

The talc was talc B.P. passed through a 200 mesh sieve to remove particles that might clog the valve (Herzka & Pickthall, 1966).

^{*} Components: Actuator button, 0.018 inch standard button; valve stem, 0.018 inch nylon stem, natural; valve housing, 0.025 inch L.D. housing, red; spring, stainless steel; gasket, standard buna gasket; dip tube, standard dip tube.

Preliminary sizing of powder samples

Talc samples were sized by Andreasen's method (B.S. 3406, 1963) using 80% ethanol as sedimentation liquid and 0.1% Lissapol as wetting agent.

Size data provided by the suppliers of the neomycin sulphate powder showed that 90% of the particles were below 10 μm , 99% below 20 μm and only single particles up to 60 μm .

No size data were available for the UFI powder but the powder was 'micronized' as a slurry in liquid propellant before pack assembly.

Calculation of particle sizes

The coefficient of drag, C_d , of a particle sedimenting in a fluid is a function of the shape of the particle and the Reynolds number, Re , of the system. For systems where Stokes' Law holds, i.e. where the Reynolds number is in the range 10^{-4} to 0.2, $C_d = 24/Re$ and the diameter of the particle may be calculated using the equation:

$$d_{st} = \sqrt{\frac{18 \eta v}{(\rho - \rho_0)g}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

(The symbols have their usual meanings.)

When the Reynolds number is in the range 0.2 to 1000 there is no constant relation between C_d and Re . The relation derived by Schiller & Naumann (1933), $C_d = 24(1 + 0.15Re^{0.687})/Re$, is reliable for Re values up to 800 (Coulson & Richardson, 1968). From this equation it may be shown that the particle diameter,

$$d^2 = d_{st}^2 (1 + 0.15Re^{0.687}) \quad \dots \quad \dots \quad \dots \quad (2)$$

A process of successive approximations was used to obtain d from equation (2). A value for the Reynolds number was obtained using the Stokes' diameter of the particle and this value was substituted together with the Stokes' diameter into equation (2) to give d . From d a second value for Re was found. From equation (2) a second value of d was thence obtained. This was repeated until successive values of d differed by less than 0.1 μm .

Heywood's tables (1948) of $\log Re$ against $\log \frac{1}{2}(C_d/Re)$ also may be used to calculate the Reynolds number and hence the diameter of a particle having a known terminal velocity and a Re value in the range 0.2 to 1000.

Both the Schiller-Naumann equation and Heywood's tables were used to calculate the diameter of particles having Reynolds numbers greater than 0.2. The diameter of particles having Reynolds number of 0.2 or less were calculated from equation (1).

Using the calculated particle sizes a cumulative weight oversize curve was derived from the kymograph recording.

The viscosity of air at the temperature of the analysis was taken from International Critical Tables (1929).

Verification of the applicability of the sedimentation column to the size analysis of particles dispersed in the top of the column

A 100 mg sample of glass beads having a nominal size range of 10–100 μm was sized by sedimentation in the column, the sample being blown into the column from a piece of metal foil using a sphygmometer pump. Two analyses were made. The beads were also sized microscopically.

Both powder and liquid pressurized sprays were sized. The powder sprays examined were talc (10%), neomycin sulphate (10%) and UFI (200 g in 300 g of propellant). n-Tetradecane was used as the test liquid for liquid spray packs because of its low volatility, low viscosity, miscibility with halogenated hydrocarbon propellants and compatibility with the valve components.

All spray size determinations were in triplicate.

The rate of hydration of the dried neomycin sulphate was so rapid that all powder entering the column was hydrated. The density of hydrated neomycin sulphate was thus used in the calculation of particle sizes. The neomycin sulphate was dried over phosphorus pentoxide in a vacuum desiccator at 60°.

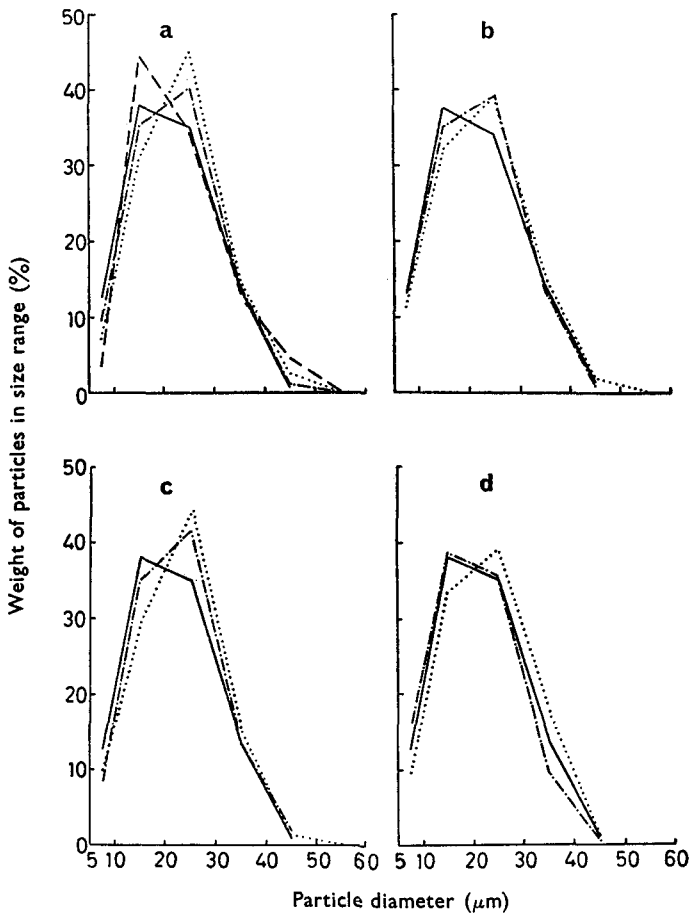


FIG. 2. Weight frequency polygons for sample I talc and sprays from packs prepared with sample I talc obtained at 20° unless otherwise stated.

a --- Andreasen's Analysis of sample I talc. — 10% talc I in Arcton 12. - · - · 10% talc I in Arcton 12 and Arcton 114 in the ratio 80:20, by weight. · · · · 10% talc I in Arcton 12 and Arcton 114 in the ratio 60:40, by weight.

b — 10% talc I in Arcton 12. - · - · 10% talc I in Arcton 12 and Arcton 114 in the ratio 80:20, and · · · · 60:40, by weight. All with vapour tap in valve housing.

c — 10% talc I in Arcton 12, 20°; - · - · at 15°; · · · · at 10°.

d — 10% talc I in Arcton 12, 20°. - · - · 10% talc I and 0.5% Arlachel 20 in Arcton 12 at 20°. · · · · 10% talc I and 0.5% isopropyl myristate in Arcton 12 at 20°.

RESULTS

Agreement between the two sets of results for the sizing of the glass beads was satisfactory (% weight of particles with diameters less than $20\ \mu\text{m}$ 0.1%, 0%; $<40\ \mu\text{m}$ 3.7%, 4.2%; $<60\ \mu\text{m}$ 72.9%, 68.5%; $<80\ \mu\text{m}$ 99.6%, 98.6%; $<100\ \mu\text{m}$ 100%; 100% measured by microscopy and air sedimentation respectively) and it was decided to use the column to size particles and drops from pressurized packs.

Comparison of the results from Andreasen's analysis of the four talc samples and from the size analysis of the talc sprays (Fig. 2a and Table 2) shows that spray size was related to the size of the talc sample used to prepare the pack. Reduction in the proportion of Arcton 12 in the propellant and lowering of pack temperature both resulted in larger talc sprays (Fig. 2a and c, Table 2).

Surfactants are sometimes added to pressurized products. Addition of 0.5% w/w of sorbitan monolaurate (Arlacel 20) to a pack containing sample I talc and Arcton 12 slightly reduced the talc spray size whereas incorporation of 0.5% w/w of isopropyl myristate resulted in an increase in spray size (Fig. 2d). Isopropyl myristate is non-volatile and is used as a lubricant to aid the passage of powder through the valve and as a suspending agent for the powder (Herzka & Pickthall, 1966).

Replacement of the valve housing by a valve housing with a 0.025 inch vapour tap in its side led to a small reduction in talc spray size (Fig. 2b).

Storage of the packs containing sample III talc led to a progressive reduction in spray size with increasing time of storage (Table 2).

Table 2. *The effect on talc spray size of propellant composition, particle size of talc sample, and storage.*

Pressurized formulation/talc sample	% Weight of particles undersize at particle diameters (μm) of:			
	10	20	30	40
Talc II; Andreasen's Analysis	5.5	33.5	76.0	91.7
10% talc II in Arcton 12 at 20°	8.9	37.7	81.4	97.8
10% talc II in Arcton 12 and Arcton 114 in the ratio 80:20, by weight, at 20°	8.8	37.4	81.0	97.4
10% talc II in Arcton 12 and Arcton 114 in the ratio 60:40, by weight, at 20°	6.7	34.4	76.8	96.9
Unsieved talc; Andreasen's Analysis	2.4	34.0	77.7	93.2
10% unsieved talc in Arcton 12 at 20°	9.1	41.3	82.9	97.5
Talc III: Andreasen's Analysis	7.2	70.5	99.9	..
10% talc III in Arcton 12 at 20°. Before storage	20.9	81.1	98.5	99.9
10% talc III in Arcton 12 and Arcton 114 in the ratio 80:20, by weight, at 20°. Before storage	17.7	73.3	98.7	99.9
10% talc III in Arcton 12 and Arcton 114 in the ratio 60:40, by weight, at 20°. Before storage	12.3	65.2	98.2	99.8
10% talc III in Arcton 12 at 20°. After 3 months storage	25.7	79.9	99.3	100.0
10% talc III in Arcton 12 and Arcton 114 in the ratio 80:20, by weight, at 20°. After 3 months storage	24.7	77.2	98.5	100.0
10% talc III in Arcton 12 and Arcton 114 in the ratio 60:40, by weight, at 20°. After 3 months storage	22.2	74.0	98.8	100.0
10% talc III in Arcton 12 at 20°. After 6 months storage	23.5	88.0	99.6	100.0
10% talc III in Arcton 12 and Arcton 114 in the ratio 80:20, by weight, at 20°. After 6 months storage	19.2	83.1	99.5	100.0
10% talc III in Arcton 12 and Arcton 114 in the ratio 60:40, by weight, at 20°. After 6 months storage	17.1	80.8	98.3	99.9

Vapour pressure (p.s.i.g.) of Arcton 12 and Arcton 114 mixtures:

100% Arcton 12 at 20°, 67.9; 15°, 56.3; 10°, 47.0.

80% Arcton 12 + 20% Arcton 114 at 20°, 59.0.

60% Arcton 12 + 40% Arcton 114 at 20°, 49.0.

The neomycin sulphate sprays were much larger than the powder used in their preparation; drying the powder before pack assembly resulted in a small increase in spray size (Table 3). The UFI powder was micronized before packaging so it seems likely that the spray particles were agglomerates of single particles. The greater the proportion of the high vapour pressure component in the propellant the smaller the UFI spray (see Table 3).

The size of the n-tetradecane sprays (Table 4) decreased as propellant concentration was increased. The use of a valve housing having a vapour tap of 0.025 inch in its side gave a marked reduction in spray size.

The behaviour of a mixture of 6.5% n-tetradecane and 93.5% light liquid paraffin

Table 3. *The effect of propellant composition on the size of UFI sprays and of drying the neomycin sulphate powder on the size of neomycin sulphate sprays.*

Pressurized formulation	% Weight of particles undersize at particle diameter (μm) of:					
	10	20	30	40	50	60
Commercial UFI pack at 20°	19.1	52.4	81.6	95.4	98.5	99.4
UFI pack containing a higher proportion of the high vapour pressure propellant component than the commercial pack; 20°	32.7	61.2	83.5	95.9	99.6	100.0
10% undried neomycin sulphate in Arcton 12 at 20° C	21.2	60.1	88.0	98.4	99.9	
10% dried neomycin sulphate in Arcton 12 at 20° C	18.1	57.0	85.2	97.9	100.0	

Table 4. *The effect on liquid spray size of propellant composition, valve structure and product viscosity.*

Pressurized formulation	% Weight of particles undersize at particle diameters (μm) of:													
	20	40	60	80	100	120	140	160	180	200	220	240	260	280
n-Tetradecane and Arcton 12 in the ratio 20:80, by weight, at 20°	20.1	80.9	97.8	99.5	99.7									
n-Tetradecane and Arcton 12 in the ratio 40:60, by weight, at 20°	1.6	28.9	70.8	90.8	97.7	99.5	99.9	100.0						
n-Tetradecane and Arcton 12 in the ratio 60:40, by weight, at 20°. Schiller-Naumann equation used to calculate the size of particles having $Re > 0.2$		0.7	5.1	13.2	25.2	41.9	58.2	70.5	81.0	88.7	93.4	97.0	99.5	100.0
n-Tetradecane and Arcton 12 in the ratio 60:40, by weight, at 20°. Heywood's tables used to calculate the size of particles having $Re > 0.2$		0.7	5.1	12.8	24.9	40.7	56.3	69.1	79.2	87.1	93.1	97.6	99.8	99.9
n-Tetradecane and Arcton 12 in the ratio 40:60, by weight, at 20°. Vapour tap in valve housing	15.4	55.5	84.7	96.1	99.3	99.9								
A mixture of 93.5% light liquid paraffin and 6.5% n-tetradecane with Arcton 12 in the ratio 40:60, by weight, at 20°	6.7	37.6	70.8	88.0	95.1	98.6	99.8	99.9						
Light liquid paraffin and Arcton 12 in the ratio 40:60, by weight, at 20°	14.6	43.3	73.5	90.6	97.7	99.6	100.0							

The mixture of 93.5% light liquid paraffin and 6.5% n-tetradecane has a viscosity of 20 cP ($20 \times 10^{-3} \text{ N s m}^{-2}$) at 20°. Light liquid paraffin has a viscosity of 27 cP ($27 \times 10^{-3} \text{ N s m}^{-2}$) at 20° and n-tetradecane a viscosity of 2 cP ($2 \times 10^{-3} \text{ N s m}^{-2}$) at 20°.

B.P. was compared with that of light liquid paraffin and that of n-tetradecane to find the effect of liquid product viscosity on spray size. The packs contained 40% liquid product and 60% Arcton 12. Increase in product viscosity led to a decrease in spray size (Table 4).

When the valves of the talc packs were taken apart it was found that powder had accumulated in the valve housings. Comparison of photomicrographs of this talc and of the talc used to prepare the packs showed that the talc from the valve housing contained a larger proportion of particles of 50 μm or more diameter.

DISCUSSION

A reduction in the internal pressure of a pack either by cooling the pack or by changing the composition of the propellant resulted in an increase in spray size. At lower pack pressures, particles suspended in the liquid propellant pass more slowly through the valve where they are subjected to less turbulence and smaller shearing forces. Propellents of lower vapour pressure volatilize more slowly and gently on leaving the valve and thus disperse the powder agglomerates less efficiently. Root (cited by Johnsen, 1961) and Lefebvre & Tregan (1964) reported similar findings for pressurized packs containing a mixed propellant and *liquid* product.

Addition of surfactant to a powder pack may reduce the interfacial tension between the powder particles and the liquid propellant and lead to a better dispersion of powder in the liquid propellant. Propellant surface tension lowering was not investigated; a pronounced effect does not seem likely as the surface tension of organic liquids is small and but little affected by surfactants. Polli & others (1969) found that addition of 0.2% sorbitan trioleate resulted in a decrease in the size of steroid aerosol particles.

Inclusion of 0.5% isopropyl myristate in a talc pack gave larger spray particles. Whilst the isopropyl myristate may marginally lower the vapour pressure of the propellant it probably exerts its action by retarding propellant vaporization and hence powder dispersion (Root, 1961).

The spray from the pack containing unsieved talc had fewer particles with diameters greater than 40 μm than did the unsieved talc used to prepare the pack. The photomicrographs of the talc from the valve housing indicated some retention of large particles. This effect could also explain the reduction in talc spray size following storage.

For packs containing liquid propellant and a miscible liquid product the higher the concentration of propellant the smaller was the liquid spray. The higher the concentration of propellant the greater the work of dispersion per unit volume of product and therefore the finer the spray produced. The propellant vapour pressure will be progressively lowered by increasing concentration of dissolved product. Hence for higher concentrations of liquid product the vaporization energy will be less and the dispersion of the product less vigorous. Lefebvre & Tregan (1964) found that for a kerosene spray having a propellant of Arcton 11 and Arcton 12 the spray became finer and more uniform with increasing propellant concentration up to 78% propellant.

By using a valve housing with a vapour tap smaller powder and liquid sprays were produced. The vapour tap enables propellant vapour to be drawn into the valve by liquid passing through the valve. Turbulence inside the valve is thus increased and spray size reduced.

No wholly satisfactory explanation can be given for the reduction in spray size associated with increased product viscosity. The viscosity of the product-propellant mixture must be related, though not necessarily directly, to the viscosity of the product. There was little difference between the surface tension values for the three liquids, determined by the Du Noüy Tensiometer, and the spray size differences cannot be explained on this basis. The three liquids may not lower the vapour pressure of the propellant the same amount but this was not investigated. Searls & Synder (1936), using an oil atomizer, showed that increasing the viscosity of the oil reduced the size of the spray drops. The amount of oil sprayed by their atomizer during any time interval decreased as product viscosity increased, i.e. as product viscosity was increased a given volume of air dispersed a smaller volume of liquid. In each of our liquid spray packs the same volume of liquid was dispersed by the same volume of propellant. Further, our observed effects of viscosity on spray size do not agree with the suggestion of Wiener (1958) and Root (1961).

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