Evaluation of Valving System Influence on the Spray Characteristics of an Aerosol Formulation Consisting of Kerosene/Propane/Butane

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The influence of formulation factors, particularly the valving system, on the spray characteristics such as spray-droplet size and delivery rate were evaluated using aerosol formulations consisting of kerosene and a mixture of propane/butane. The liquid/propellant ratio was fixed at 60/40 by weight and the pressure of the propellant was 4.8 kg/cm^2 (gauge) at 20 °C. The spray-droplet size was measured by using the laser-diffraction drop-sizing method. The sizes of the three orifices in the valving system (stem orifice [ST], vapor-phase tap orifice [VT] and actuator orifice [BU]) affected both the spray-droplet size and the delivery rate. The bigger the size of ST and BU and the smaller the size of VT, the greater the delivery rate. The spray-droplet size was affected by the mutual interactions among ST, BU and VT. The spray-droplet size decreased as the size of VT increased when ST was larger than BU or was not much smaller than BU. The effect of VT to reduce spray-droplet size did not appear when BU was too much larger than ST. When VT was small enough or absent, the smallest spray-droplet size was obtained when the ST/BU ratio was around one. When VT was large, the spray-droplet size decreased as the ST/BU ratio increased. It was concluded that the balance of sizes of the three orifices was very important to obtain the most suitable spray characteristics.

Keywords aerosol formulation; spray characteristics; spray-droplet size; delivery rate; propellant pressure; liquid/propellant ratio; orifice size; valving system; stem orifice; vapor-phase tap orifice; actuator orifice

The spray characteristics of an aerosol formulation are very important to obtain optimum performance. Among them, the spray-droplet size and the delivery rate are the most important properties for space-spray aerosols such as air fresheners, insecticides, *etc.*[1] Although it is well known that these properties are affected by formulation factors such as propellant pressure, liquid/propellant ratio and size of orifices in the valving system,[2,3] little is known about how to control the spray characteristics of an aerosol formulation by using these factors. Murayama *et al.*[3] reported the influences of the formulation factors on the spray-droplet size of aerosol formulations and concluded that the formulation factors mentioned above had an interactive influence on the spray-droplet size. They analyzed the interactive effect of three orifices (stem orifice [ST], vapor-tap orifice [VT], and actuator orifice [BU]) in the valving system of an aerosol formulation and showed that the size ratios of VT/BU and VT/ST had a linear relationship with the spray-droplet size, which showed a tendency to decrease in inverse proportion.

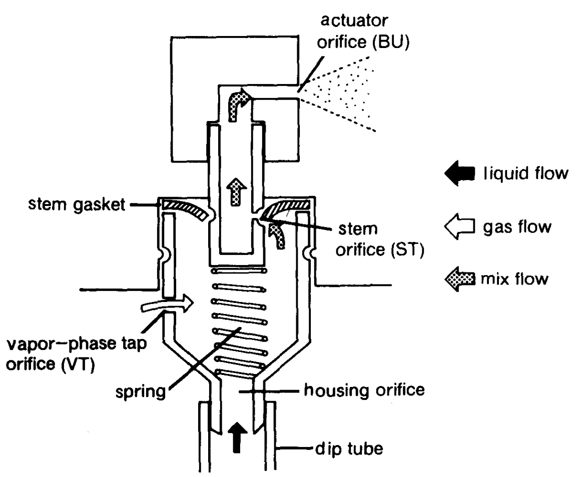

Fig. 1. A Cross-Sectional Diagram of a Valving System

Recently, several new technologies to measure spray-droplet size have been developed in connection with research on internal combustion engines.[4] These new technologies allow us to obtain a large number of data in a relatively short time. Laser-diffraction drop-sizing is one of such methods, and is most commonly used in research on liquid atomization technology.[4a–e] In this study, we re-examined the effect of the formulation factors, particularly the size of the orifices in the valving system, on the spray-droplet size of aerosol formulations by using a laser-diffraction drop-sizing instrument. The data are compared with those obtained by Murayama *et al.*,[3] who measured the droplet size by using optical microscopic sizing of droplets collected on a Teflon-coated slide glass. The delivery rate was also determined to allow discussion of the overall properties of aerosol formulations.

Experimental

Materials Neochiozol®[2a] (deodorized kerosene supplied by Chuo-kasei Co., Ltd.) was used as the system liquid and two mixtures of propane/butane (pressures were 3.6 and 4.8 kg/cm^2 (gauge) at 20 °C) were used as the propellants. The valving systems used in this experiment were supplied by Precision Valve Japan Co., Ltd. Figure 1 shows a cross-sectional diagram of an aerosol valve.

Preparation of Aerosol Formulations When the effects of the pressure of propellant and the liquid/propellant ratio were evaluated, the dimensions of the valving system were fixed as BU 0.33 mm, ST 0.33 mm, VT 0.33 mm and housing orifice 2.03 mm. When the effect of the valving system was analyzed, propellant of 4.8 kg/cm^2 (gauge) at 20 °C was used and the liquid/propellant ratio was fixed at 60/40 by weight.

Measurement of the Inner Pressure The inner pressure of an aerosol formulation was measured at 25 °C by using a pressure gauge attached to the stem of the valve.

Measurement of the Delivery Rate The delivery rate of an aerosol formulation was determined at 25 °C, by measuring the weight decrease of the aerosol after spraying continuously for 5 s.

Measurement of the Diameter of Spray Droplets The diameter of spray droplets was measured by using a laser-diffraction drop-sizing instrument (Malvern particle sizer, model 2200; Malvern Co., Ltd., England).[4a,b] The aerosol was sprayed 30 cm from the laser beam. All the droplet size data in this report are expressed as the *PE* value by the use of Rosin–Rammler's distribution equation (see below), which is reported to be one of the most suitable distribution equations to apply to the droplet size distribution of a liquid spray.[5)]

$$S = e - (D/PE)^{w}$$

where S = a fraction of droplets smaller than diameter D (μm), PE = a characteristic fraction where $1/e$ or 36.8% w/w of the droplets is larger in diameter than PE (μm), W = a measure of the spread of the droplet size distribution, D = diameter (μm) of the droplets, e = exponential.

The PE value can be used as a representative value of droplet size distribution, though it is not equal to the volume median diameter. In this report, the PE value is meant when the term "the diameter of spray droplets" is used.

Results and Discussion

Effect of the Pressure of Propellant and the Liquid/Propellant Ratio Figure 2a shows the relationship between the delivery rate and the liquid/propellant ratio using two kinds of propellants. The delivery rate did not change very much when the liquid/propellant ratio was varied from 20/80 (w/w) to 80/20 (w/w). The pressure of the propellant had little effect on the delivery rate. Figure 2b shows the relationship between the inner pressure and the liquid/propellant ratio. The higher the liquid/propellant ratio and the lower the pressure of propellant, the lower the inner pressure. Figure 2c shows the relationship between the diameter of spray droplets and the liquid/propellant ratio. The liquid/propellant ratio definitely affected the diameter of spray droplets whereas the pressure of propellant had little effect on the spray-droplet size. These results coincide with the results of Murayama *et al.*[3a,e)] It is

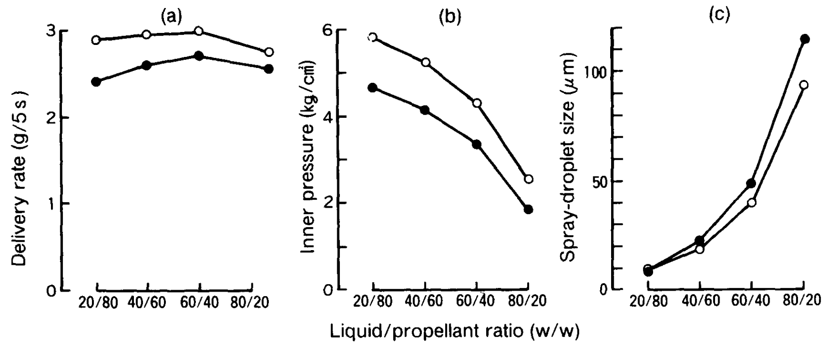

Fig. 2. Effects of the Liquid/Propellant Ratio and the Pressure of Propellant on the Physical Properties of Aerosol Formulations
Pressure of propellant: ●, 3.6 kg/cm² (gauge) at 20 °C; ○, 4.8 kg/cm² (gauge) at 20 °C.

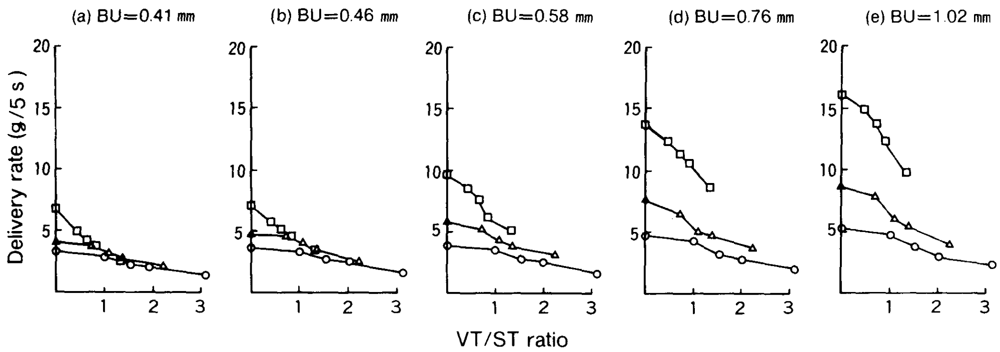

Fig. 3. Effect of VT/ST Ratio on the Delivery Rate of Aerosol Formulations
ST: ○, 0.33 mm; △, 0.46 mm; □, 0.76 mm.

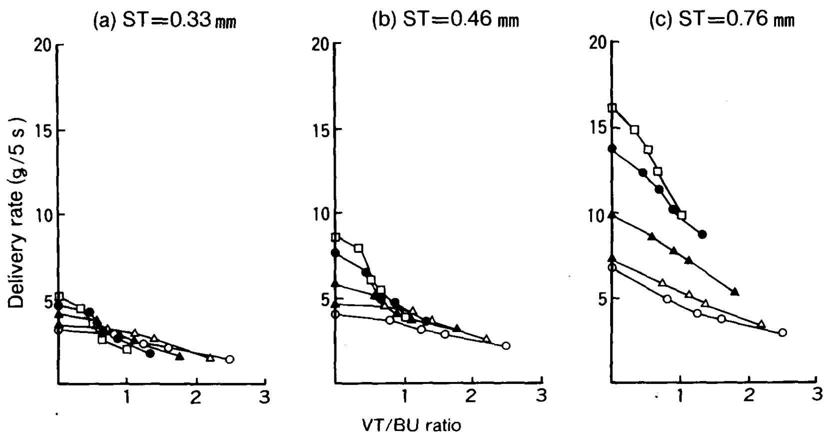

Fig. 4. Effect of VT/BU Ratio on the Delivery Rate of Aerosol Formulations
BU: ○, 0.41 mm; △, 0.46 mm; ▲, 0.58 mm; ●, 0.76 mm; □, 1.02 mm.

said that fine spray droplets are made through the flashing of coarser spray droplets delivered from the spray nozzle by the rapid gasification of the propellant (liquified gas).[1d] Consequently, the spray droplets are efficiently made finer as the proportion of the propellant increases.

Effect of the Valving System on the Delivery Rate The effect of the valving system on the delivery rate was analyzed by using three parameters, the VT/ST, VT/BU and ST/BU ratios. Figures 3 and 4 show the effects of VT/ST and VT/BU, respectively. The plots on the ordinate show the data when VT=0. The delivery rate decreased as these ratios increased. As shown in Fig. 1, VT is an orifice located at the vapor phase in an aerosol system. The delivery rate of the vapor phase increased as the orifice size of VT was increased — the larger VT, the greater the release of gaseous propellant. Figure 5 shows the effect of ST/BU. The delivery rate decreased when both ST and BU were decreased in size.

Effect of the Valving System on the Spray-Droplet Size Figures 6,7 and 8 show the effect of VT/ST, VT/BU and ST/BU ratios on the spray-droplet size, respectively. Figure 6 indicates that VT has the effect of making spray droplets finer when BU is smaller than ST. When BU is large, VT has almost no effect in making spray droplets finer. Figure 7 indicates that VT has the effect of reducing the spray-droplet size when ST is large but does not always

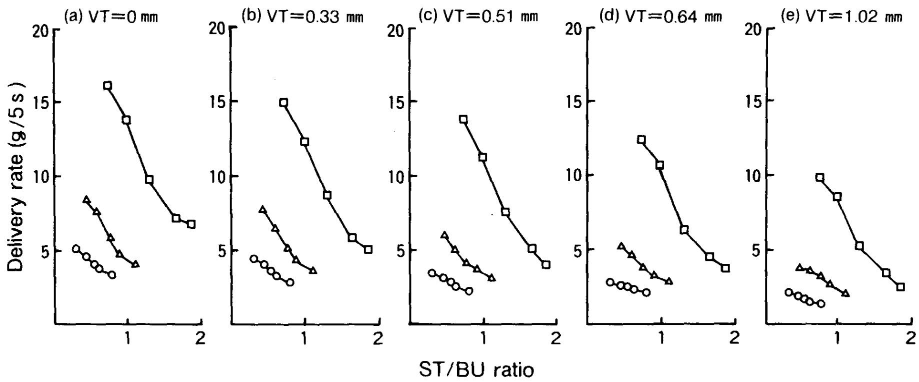

Fig. 5. Effect of ST/BU Ratio on the Delivery Rate of Aerosol Formulations
ST: ○, 0.33 mm; △, 0.46 mm; □, 0.76 mm.

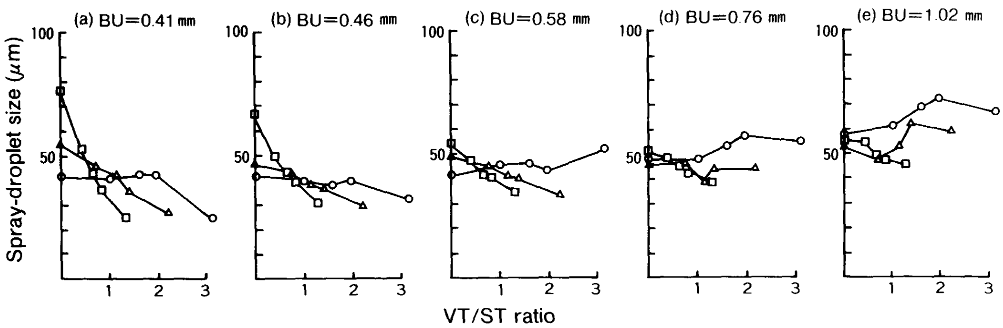

Fig. 6. Effect of VT/ST Ratio on the Spray-Droplet Size of Aerosol Formulations
ST: ○, 0.33 mm; △, 0.46 mm; □, 0.76 mm.

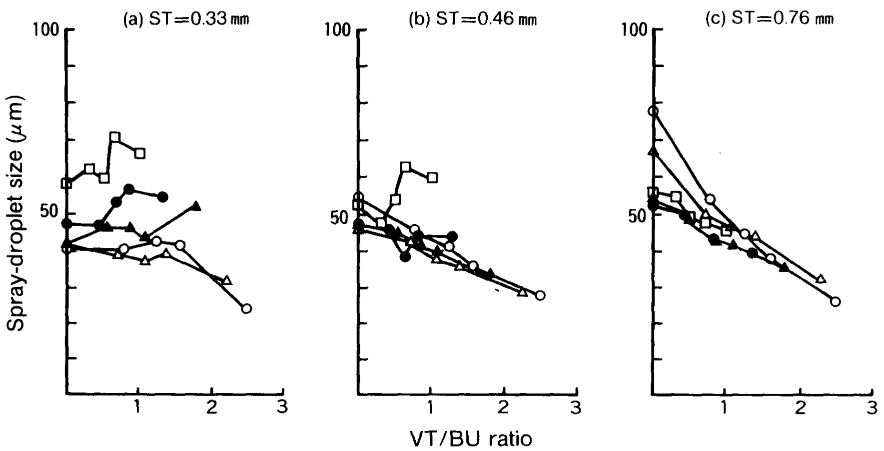

Fig. 7. Effect of VT/BU Ratio on the Spray-Droplet Size of Aerosol Formulations
BU: ○, 0.41 mm; △, 0.46 mm; ▲, 0.58 mm; ●, 0.76 mm; □, 1.02 mm.

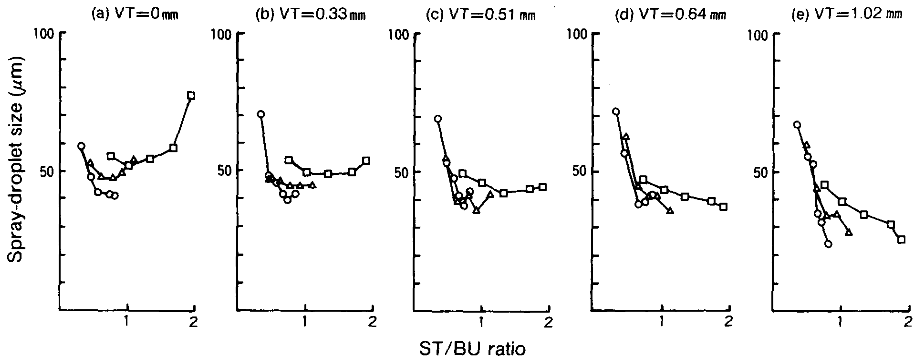

Fig. 8. Effect of ST/BU Ratio on the Spray-Droplet Size of Aerosol Formulations
ST: ○, 0.33 mm; △, 0.46 mm; □, 0.76 mm.

have such an effect when ST is small. It was also found that VT reduces the spray-droplet size when ST is not much smaller than BU. Figure 8 shows the effect of ST/BU on the spray-droplet size. When VT is large, the smaller the ratio of ST/BU (or the smaller the size of ST in comparison with that of BU), the bigger the spray-droplet size. However, in cases where there is no VT, or VT is too small, the smallest spray-droplet is obtained when ST/BU is around one. The results we obtained can be summarized as follows:

1. The size of spray droplets decreases as the size of VT increases, when ST is larger than BU or is not much smaller than BU.
2. The effect of VT to reduce spray-droplet size does not appear when BU is too much larger than ST.
3. When VT is small enough or absent, the smallest spray-droplet size is obtained when ST/BU is around one.
4. When VT is large, the spray droplets decrease in size as ST/BU is increased.

Many of our results coincide with the results obtained by Murayama *et al.*[3f] although the methods used to measure the droplet size and the distribution equations used to obtain the mean droplet size were different. However, one of our new findings is that the spray-droplet size does not change or even increases as the ratios of VT/ST and VT/BU increase in the case that the ratio of ST/BU is small. Murayama *et al.* concluded in their report[3f] that there was a tendency that the spray-droplet size decreased as the ratios of VT/ST and VT/BU increased. According to our results, this tendency is observed only when the ratio of ST/BU is large. The difference between the two conclusions does not seem to be significant because the conclusion of Murayama *et al.* was based on analysis of the averaged data obtained from experiments with an orthogonal array design, *i.e.* the effect of ST/BU ratio is averaged. Another new finding is that the balance of ST and BU is important to obtain fine spray droplets when VT is small. A similar result was reported by Fulton *et al.*,[6] who showed that the most uniform sprays were obtained when the ratio of the inlet (ST) and outlet (BU) diameters was about 2:3.

As shown in Fig. 1, the four orifices in a valving system each have distinct functions. The housing orifice introduces the liquid substance *via* the dip-tube which reaches the bottom of the aerosol formulation. VT is an orifice which introduces the gaseous propellant in the housing part of the valve. It is thought that the rapid flow of the gaseous propellant, which is introduced through VT and mixed with the liquid flow from the housing orifice, helps the atomization of the liquid at BU as if BU were a twin-fluid-type nozzle. ST is an orifice which performs the "open and shut" function of the valve. BU is an orifice which atomizes the liquid into the air. The space between ST and BU is called "an expansion chamber" and is known to have value in promoting small spray-droplet size.[7] Considering these functions of the orifices, the results mentioned above can be explained as follows:

1. When ST is larger than BU, BU limits the total flow rate in the valve, so that there is little loss of pressure before the liquid is atomized through BU. In this case, it is thought that the liquid atomization at BU becomes more efficient as the size of VT is enlarged due to the effect of gaseous propellant supplied from VT; the gasified propellant helps the atomization of the liquid at BU as if BU were a twin-fluid-type nozzle. When ST is almost equal in size to BU, or is not much smaller than BU, the reduction of the pressure between ST and BU is thought to be small, so that the effect of VT to reduce the spray-droplet size is thought to be maintained.

2. When BU is much larger than ST, ST limits the total flow rate in the valve. The pressure of the liquid is then greatly reduced after it has passed through ST. In this case, if VT is enlarged, the amount of liquid flow which passes through ST decreases, and the pressure of the liquid, after it has passed through ST, is much reduced. Consequently, BU can not atomize the liquid efficiently due to the reduction of the pressure; thus the spray-droplet size increases as the size of VT is enlarged.

3. When VT is small enough or absent, there is little or no supply of gaseous propellant from VT. In the case of an aerosol formulation, the liquefied gas which is mixed with the solvent in the formulation has high vapor pressure by itself. When BU is larger than ST (ST/BU is smaller than one), a part of the liquefied gas is thought to be gasified in the expansion chamber between ST and BU due to the reduction of the pressure, and helps the pulverization at BU, somewhat like a twin-fluid-type nozzle. This effect, however, is thought to act inversely when ST/BU is too small (ST is too much smaller than BU) because the pressure of the liquid after it has passed through ST is reduced too much. Consequently, the optimum ratio of ST/BU is thought to be around one; at this ratio, there would not be much reduction of the pressure, and BU can act as a twin-fluid-type nozzle most efficiently. However,

when ST is larger than BU (ST/BU is larger than one), the reduction of the pressure after the liquid passes through ST is going to be smaller. BU is then more likely to act as a mono-fluid-type nozzle and the spray-droplet size increases as the ratio of ST/BU is increased to more than around one.

4. When VT is large, the valve always acts as a twin-fluid-type nozzle; the smaller the size of BU or the larger the ratio of ST/BU, the smaller the spray-droplet size.

This report describes the effect of the formulation factors on the spray characteristics of an aerosol formulation. Many of the results obtained in this study coincide with the results obtained by Murayama *et al.*[3] The most interesting finding of this work is the fact that ST, BU and VT interact in a complex manner to influence the spray-droplet size of aerosol formulations. For example, the balance of ST and BU is extremely important to obtain fine spray droplets when VT is small. Also it is noteworthy that VT does not always act to reduce spray-droplet size. It is concluded that the balance of the sizes of the three orifices is extremely important to obtain the most suitable spray-droplet size and delivery rate at the same time.

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