

Natural Pulsations in Electrical Spraying of Liquids

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The production of charged heavy particles by the electrical spraying of glycerine and Octoil from the tip of a metal capillary has been examined experimentally at voltages below about 4 kv. The current produced by the low-voltage spraying generally appears in the form of one or more sets of naturally occurring periodic pulses. The width, amplitude, period, and shape of the current pulses are discussed in terms of the applied voltage, liquid pressure, spacing between capillary tip and accelerating electrode, and temperature effects. Techniques for relating a certain set of current pulses to its corresponding spray jet along the axis or around the periphery of the capillary tip and for still photomicrography of the liquid surface at any instant before, during, and after the natural spraying pulse are described. Mention is made of the variation of specific charges produced at different intervals during the natural pulsations as measured by a time-of-flight mass spectrometer, and a method is indicated whereby the spraying pulses can be synchronized externally.

Introduction

ELECTRICAL spraying is the process whereby the application of a sufficiently high electric field to the liquid emerging from a fine capillary tube causes the liquid to disperse into numerous small droplets or charged heavy particles. Also known as electrical atomization and electrical dispersion, the process basically is one that involves an instability at a liquid interface owing to electrostatic forces, produced by induced surface charges, overcoming the cohesive forces of the liquid. The requisite surface charge can be produced by allowing the liquid in question to emerge under pressure from the end of a metal capillary maintained at a positive d.c. voltage with respect to an associated ground plate or accelerating electrode. The minimum value of voltage required to initiate electrical spraying is called the minimum spraying voltage. The liquid pressure is insufficient to cause a liquid jet in the absence of the applied voltage.

The electrical spraying action apparently was discovered by Bose‡ in 1745. It was rediscovered in 1914 by Zeleny^{2,3} who studied the phenomenon extensively over a period of many years from the standpoint of the discharge from a liquid point. Vonnegut and Neubauer⁴ studied electrical spraying for the production of monodisperse liquid particles, and Drozin¹ examined electrical dispersion of dielectric liquids. Various factors, which influence electrical spraying have been described in this country⁵ and abroad,⁶ and recent photomicrographs have revealed some details of the spraying mechanism.⁷

A criterion for the instability of a charged liquid droplet was established in 1882 by Lord Rayleigh.^{8,9} Details of this criterion have been clarified recently by Hendricks and Schneider,¹⁰ and the theory has been applied to the case of a nearly hemispherical liquid droplet at the tip of a metal capillary.⁷ Additional insight into the spraying process has been provided by Taylor¹¹ who showed that internal pressure

is not the same as that outside the drop when instability occurs.

Undoubtedly all of these investigators have noted the existence of several modes of spraying which varied from the naturally pulsed to the steady axial spraying and to the cone-shaped spray. Paucity of literature on the natural pulsations of low-voltage spraying indicates that only a small amount of study has been devoted to the process. Zeleny^{2,3} was probably the first to mention the regular pulsations and concluded that many millions of droplets are sprayed per second. In 1959, Pierce¹² allowed the drops produced by the pulsating spraying to form regularly spaced spots on moving blotter paper, and he confirmed the pulsation period by oscillographic observations of the current pulses. Pierce concluded from his measurements that only a very small number of drops were sprayed per second which corresponded to the pulsating frequency. One purpose of this work, based on numerous measurements of the naturally pulsed spraying regime, is to clarify the opposing conclusions of Zeleny and Pierce.

Natural Pulsations

The electrical spraying of liquids from a metal capillary in vacuo (5×10^{-6} torr) for voltages at and slightly above the required minimum spraying voltage is generally pulsating in nature and features the liquid necking down into a slender axial filament. Charged heavy particles apparently are sprayed from the end of the liquid filament where a portion of the liquid surface becomes unstable and disintegrates into many charged droplets. The basic components of the experimental system are illustrated in Fig. 1.

The study of the natural pulsing was greatly facilitated by monitoring the current, which accompanied each burst of sprayed particles. The current was measured conveniently by observing the voltage across a 1-meg resistor inserted in series with the accelerating electrode. The current to other nearby grounded components may be assumed negligible if the accelerating electrode is sufficiently close to the spraying capillary. Since charged droplets were sprayed axially at low voltages, their entry into the time-of-flight mass spectrometer was readily controlled by pulsing off the positive voltage applied to the control electrode.

The pulsations produced by spraying glycerine and Octoil were strongly dependent upon the applied voltage. Measurements were made at ordinary room temperature which

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related the applied voltage to the amplitude, period, and width of the current pulses for various spacings between capillary tip and accelerating electrode and for different liquid flow rates. Typical results are reproduced in Fig. 2 for spraying glycerine with a spacing of 5 mm between capillary tip and accelerating electrode and for flow rates between about 10^{-10} kg/sec and a maximum of 10^{-9} kg/sec. The results for Octoil were similar in form. The stainless-steel capillary was etched in a solution of acetic acid and chromium trioxide so that it possessed a smooth periphery of 0.1 mm in diameter.

It is observed from Fig. 2 that, as the applied voltage was progressively increased above the minimum spraying voltage of about 2.4 kv, the pulse period and width both decreased, with the period initially decreasing more rapidly than the width, and the amplitude went through a minimum and then a maximum before decreasing rapidly. Although not shown in Fig. 2, it was also found that at a certain critical voltage near 3.5 kv, when the period-to-width ratio approached about 3.0 (with the width near 3 msec), the pulsations suddenly ceased, the current became constant, and no spraying was observed. As the applied voltage was increased above the critical voltage, the current pulses reappeared in sets, generally unequal in amplitude, width, and period, becoming progressively smaller in amplitude and width but more numerous until the current finally looked like a jumble of noise.

At voltages below the critical value of 3.5 kv, the spray was observed to be along or near the axis of the capillary, and it originated from liquid adhering to the capillary. At voltages above the critical value of 3.5 kv, the spray was observed to occur as one or more jets, which originated around the periphery of the capillary rather than along the axis, and no liquid adhered to the capillary.

Figure 2 shows that increasing the liquid flow rate had only a relatively small effect on the amplitude and width of the current pulses, but decreased the period markedly.

In all of the cases, the pulse period increased rapidly as the applied voltage was reduced toward a certain minimum value. This allowed a minimum spraying voltage to be defined as that low voltage for which the extrapolated curve of pulse period apparently became asymptotic. Details of this situation are presented in Fig. 3 for several spacings. It is noticed that, as the spacing between the capillary tip and accelerating electrode was increased in steps, the minimum spraying voltage and the critical voltage increased, and similar pulse amplitude, width, and period values were obtained, but for higher applied voltages at each step. Calculations indicated that the minimum spraying voltages thus determined were nearly directly proportional to spacing over the range of values tried. Other measurements indicated that the minimum spraying voltage decreased as liquid flow rate increased.

When additional light from a microscope illuminator was focused on the tip of the spraying capillary, it was noticed after a certain time delay that the width and period decreased, and the amplitude increased. Measurements indicated that

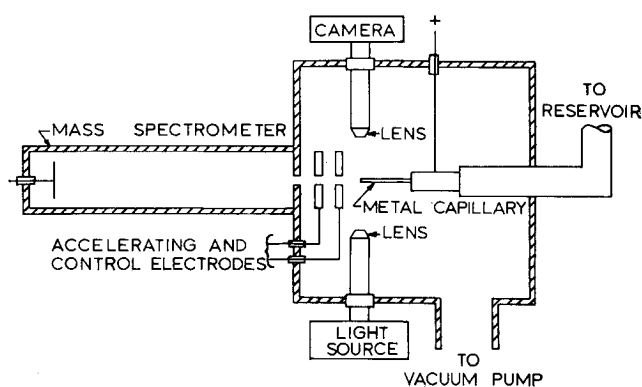


Fig. 1 Basic components of the experimental system.

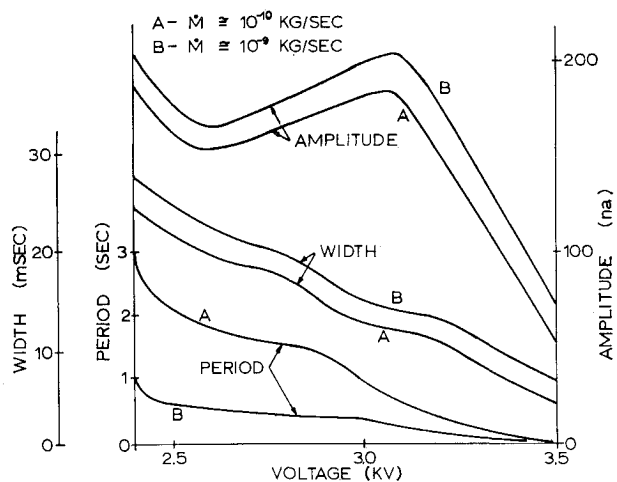


Fig. 2 Influence of accelerating voltage and mass flow rate on the spraying pulses of glycerine.

the constant lighting increased the temperature at the capillary tip by about 30°C . The changes in the pulsations were probably produced by the increased temperature rather than by a photoeffect because it required a time delay of about 1 min before a new steady-state pulsing regime became established.

To determine the influence of heat in the absence of additional light, direct current was passed through a heater coil slipped over the capillary and insulated from it electrically. It was found that, for constant values of applied voltage and liquid flow rate, the pulse width and period decreased almost exponentially as the square of the heater current increased. The minimum spraying potential also decreased for progressively higher values of heater current. The pulse shape changed significantly from its usual form. Certain combinations of voltage, liquid pressure, and heater current produced pulses with steep sides and either increasing, constant, or decreasing amplitudes.

Photomicrography

Owing to the fact that additional constant light caused drastic changes in the spraying process, the use of a high-speed movie camera with its associated high-intensity light source was rejected for photographic purposes. Instead, the current pulses were used to trigger, after any desired delay time, a Strobotac light source of short time duration. This technique made possible the viewing and still photomicrography of the liquid surface at any desired instant before, during, or after a natural spraying pulse and the identification of a liquid surface with its instantaneous spraying current.

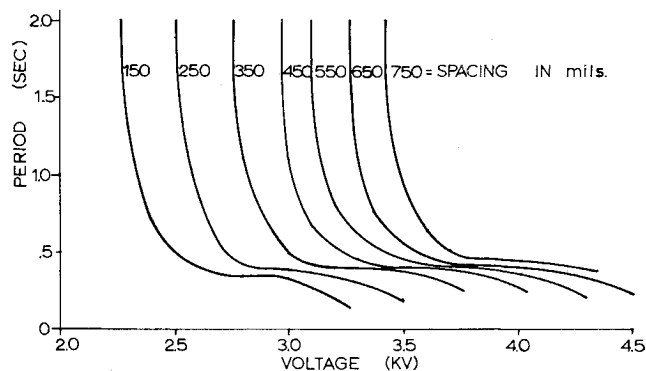


Fig. 3 Influence of accelerating voltages and spacing on pulsing period of glycerine.

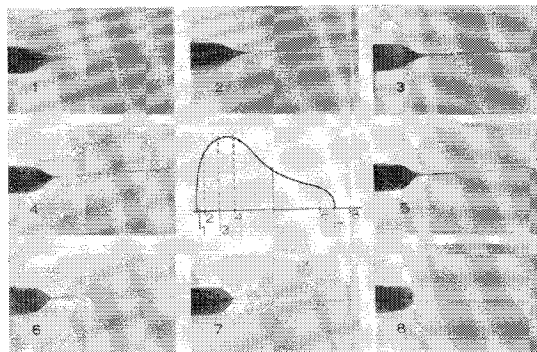


Fig. 4 Typical liquid contours related to corresponding instants during the current pulses of spraying glycerine (pulse width = 19 msec).

The time duration of the light flash was sufficiently short so that it did not influence the spraying process.

By synchronizing the light flash with a certain current pulse, the physical position of its corresponding spray jet along the axis or around the periphery of the capillary tip could be observed provided that the spray was not too fine. The series of retouched photomicrographs in Figs. 4 and 5 relate the liquid surfaces to the resulting current produced by each spraying pulsation. The indistinctness of the liquid surfaces was probably caused by motion during the light flashes rather than by vague surfaces.

The shapes of the current pulses are not very well understood. The current pulses for spraying Octoil were particularly complicated since additional current pulses (not present in Fig. 5) also occurred at an extremely low rate and were superposed on those shown.

The low-field d.c. conductivity of glycerine was 5×10^{-7} mho/cm and was about 10^{-11} mho/cm for Octoil. This difference probably accounts for the fact that the amplitude of the current pulse for Octoil was about 500 times less than that for glycerine and was nearly 0.4 nanoamp.

A proportionality was observed generally between the diameter of the liquid filament and the amplitude of the current. It was also found that no liquid filament or sprayed droplets could be seen whenever the current was constant, such as near the end of the current pulse for Octoil (shown in Fig. 5) or at the critical voltage referred to previously.

Time-of-Flight Mass Spectrometry

The successful operation of a time-of-flight mass spectrometer requires that the charged particles enter the spectrometer in groups rather than continuously. Although the low-voltage spraying is naturally pulsating, which automatically groups the charged particles, the pulse duration is too great to permit better than a rough approximation of the drift time of individual charged particles. Thus it was necessary to employ a control electrode at the entrance of the spectrometer so that charged particles entered the spectrometer only during the time a control pulse was applied. The drift time was then accurately measured when the control pulse was narrow. The control pulse was varied in position relative to the spraying pulse in order to investigate the specific charges of the sprayed particles emitted at various intervals during the spraying pulses.

If the drift space of the spectrometer is sufficiently long, the charged particles will be separated timewise into discrete bunches according to their specific charges. Output voltage pulses, corresponding to individual bunches as they impinge on the collector plate, were obtained across a 1-meg resistor.

It was observed, in general, that the specific-charge spectrum produced by one spraying pulse was nearly always different in distribution from the spectrum for another spraying pulse. The spectrum spread for a particular set of operating

conditions was obtained by taking multiple-exposure photographs of the spectra produced by several spraying pulses.

The drift times of the sprayed droplets depended upon which portion of the spraying pulse was examined. These data are shown in Fig. 6 for a 90-cm drift space. The drift times obtained for particles sprayed at the peaks of the current pulses were longer and more widely spread in values than at the beginning and end of the current pulses. Thus, the sprayed particles had higher and more uniform specific charges at the beginning and end of the spraying pulses than at other times during the spraying pulses. Individual specific charges ranged from about 0.2–7 coul/kg.

When additional light from a microscope illuminator was focused on the tip of the capillary while spraying glycerine, it was noticed that the drift times decreased, as the pulse width and period gradually increased, until a new steady-state situation was obtained. This indicated that the specific-charge values increased by about five times in a particular case. It is possible that the increased temperature caused more rapid evaporation of the sprayed droplets. The behavior of evaporating charged droplets has been studied by Doyle et al.¹³

The output of the spectrometer decreased rapidly into the noise level as the applied voltage was increased by only a few hundred volts above the minimum spraying voltage. For this reason, no measurements were made to relate specific charge to applied voltage near or above the critical voltage. This difficulty can perhaps be eliminated in future work by using an amplifier with a significantly lower noise level, by focusing or deflecting the sprayed particles or by mechanically orienting the capillary so that the sprayed particles strike the collector plate, and by using a shorter drift space.

External Synchronization

It is possible to produce more uniformity in specific charge by removing the applied voltage just after a spraying pulse commences. This prevents the formation of the lengthy liquid filament of which the radius varies greatly during a spraying pulse and so eliminates the resulting widely varying specific charges, which would have been produced during the removed portion of the spraying pulse. When the positive capillary voltage was reduced to zero by application of a negative pulse, it was also found that the natural pulsing could be synchronized by external means.

Each instant during a natural spraying pulse required a certain minimum width for the negative pulse to force the termination of that particular pulse. This indicated that a definite time was necessary for the surface charge and liquid shape to relax back to a nonspraying condition. For example, assume a typical spraying situation for which the pulse width

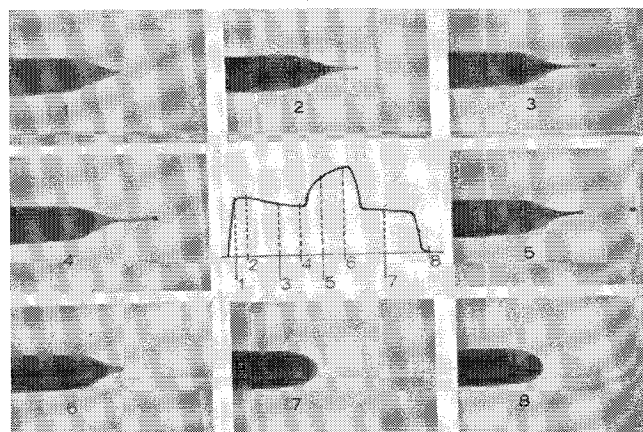


Fig. 5 Typical liquid contours related to corresponding instants during the current pulses of spraying Octoil (pulse width = 3 msec).

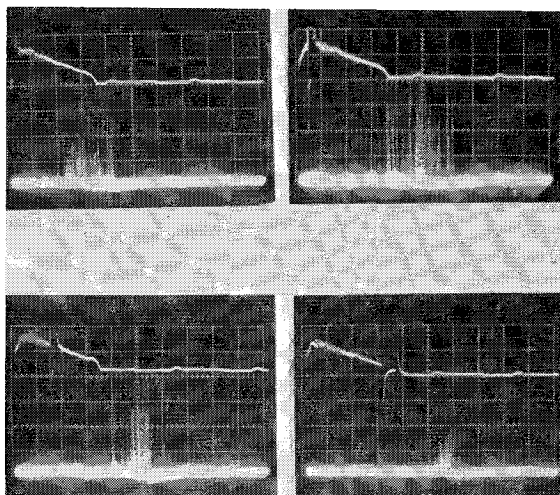


Fig. 6 Typical specific-charge spectra produced during selected intervals of the current pulses for spraying glycerine.

is 19 msec and the period is almost 1000 msec. When the negative pulse is applied 15 μ sec after the spraying pulse is started, it has to be 200 μ sec in duration to stop that particular pulse. Immediately after this negative pulse ended, the next regular spraying pulse started with no observable change in shape, width, or period for all of the succeeding spraying pulses. If the width of the negative pulse was increased to 1 msec, the next regular spraying pulse occurred 30 msec after the end of the negative pulse, rather than immediately after as before.

When the negative pulse occurred at the peak of the spraying pulse, it had to be 0.7 msec in duration in order to stop that spraying pulse. The next regular spraying pulse appeared 250 msec later. Increasing the width of the negative pulse to 10 msec simply delayed the next regular spraying pulse by about the same amount. Delaying the negative pulse to later instants during the spraying pulse required a correspondingly smaller width to stop that particular spraying pulse, the pulse period becoming progressively longer.

It has been demonstrated that the period of the spraying pulses can be controlled by the negative pulses. By adjusting the width and repetition rate of the negative pulses, the period and width of the spraying pulses can be varied at will over a wide range. The process also allows the specific charges of the emitted particles to be higher and more uniform in value.

Summary

It has been found that the current resulting from electrical spraying was sensitive to all of the variables involved with the spraying process. The simple technique of observing the spraying current allowed several different spraying modes to be identified which depended upon the applied voltage. At low voltages, regularly recurring pulsations of the liquid surface occurred, and the pulsation period was readily confirmed by oscillographic observations of the current. Measurements of the pulse period allowed a minimum spraying voltage to be defined and related to electrode spacing and liquid flow rate. The influences of light and heat on the spraying phenomena were readily detected by current measurements.

The current pulses were used to trigger a light source of short duration. This eliminated the photographic uncertainty of catching the liquid surface when it was actually spraying and allowed a certain set of current pulses to be associated with the physical position of its corresponding spray jet.

Time-of-flight mass spectrometry was successfully used to determine the specific-charge spectra for the low-voltage naturally pulsed spraying mode. The spraying current was again useful in showing that the sprayed particles had higher and more uniform specific charges at the beginning and end of the spraying pulses than at other times during the spraying pulses.

It has been shown that a very large number of droplets were emitted during each spraying pulse. This supports the early conclusion of Zeleny and contradicts the findings of Pierce. It cannot be assumed that each current pulse is composed only of one sprayed drop plus the spherule formed from the originally interconnecting thread of liquid between the liquid mass and the drop. If Pierce had allowed the sprayed droplets to impinge on a fast-moving blotter paper, it is likely that he also would have observed the large number of droplets per spraying pulse.

By pulsing off the applied voltage shortly after a spraying pulse commences, the widely varying specific charges during the remainder of that spraying pulse were eliminated. Not only did this produce more uniformity in the resulting specific charge, but also it allowed the natural pulsing to be synchronized by external means. This could prove to be of some future value when the spray from several capillaries is to occur in some desired order.

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