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Observation of Coffee Ring Transformations Under the Influence of Nanosecond Electrical Discharges in Drying Drops

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In this paper, the influence of pulsed-periodic sequence of nanosecond electrical discharges on drying drops of coffee was examined. In the absence of discharges the well-known "coffee ring effect" on metal foil was observed. However, after exposure to discharges, the stain of dried droplets had another look and structure. The fundamental significance of the work is to provide a new method of controlling of coffee rings by using nanosecond repetitively pulsed electric discharges affecting the top of the drying droplets. In particular, it turned out that the coffee particles were distributed more evenly over the area of the stain due to electrohydrodynamic flows that occur in the drop under the action of discharges. This effect can be used, for example, in inkjet printing.

Keywords: Drying drop, coffee ring effect, electric discharge

1 INTRODUCTION

In colloidal matter physics there is the well-known "coffee ring effect", which is as follows. In the process of coffee drop drying landed on a flat, wettable surface, its edge is 'fixed' on this surface and the reduction of liquid volume during drop evaporation is not accompanied by a decrease of the radius but the

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height of the drops. As a result, a capillary fluid flow is established in the drop from the center to the edge, and this flow drags particles suspended in the drop of coffee. When evaporation ends, the same “coffee ring” in stain pattern – a circular cluster of particles remains on the surface [1]. It is clear that not only coffee particles can act as micro- and nanoparticles suspended in the fluid.

In the last decade, a huge number of publications devoted to this effect has been published. The popularity of “coffee ring effect” for researchers can be explained by the following reasons. First, the simplicity and accessibility of the research object is evident even for school laboratories. Secondly, there are numerous applications of the effect in the inkjet printing, in the technology of electronic circuits [2–3], as well as in medicine [4]. Thirdly, the effect is within one of the modern trends in physical chemistry research that is the science of formation of complex micro-patterns and the growth of crystals in the drying colloidal droplets [5-8].

One important area of research is the search of physical mechanisms that suppress the “coffee ring effect” or control this effect. For example, it was reported that the effect may be suppressed by using elongated particles [9]. It may also be achieved by using acoustic impact on the drying droplet [10] or by the method of simultaneous adsorption and a long-range interaction of particles [11].

The suppression of the effect is also carried out at the expense of the electric control of contact angle of drops on the surface. To do this, a needle electrode is immersed into the drop and variable voltage amplitude of up to 200 V at a frequency of 6 Hz to 100 kHz [12] is applied to it. The paper [13] provides the review of the control methods. It should be taken into consideration that practically all of them are based on the change of drying drop fluid flow geometry.

In this paper, a new method of controlling dried drop stain patterns with the help of periodic nanosecond pulse electric discharges affecting the top of the coffee sessile drop was investigated. It is found that after exposure to discharges the stain of dried droplets had another appearance and structure. It turned out that the coffee particles were distributed more evenly over the area of the stain due to electrohydrodynamic flows that occur in the drop under the action of discharges. This effect can be used, for example, in inkjet printing.

2 MATERIALS AND EQUIPMENT

In the research ground roasted coffee ‘Jacobs Monarch’ produced by ‘Mondelez Bulgaria Production Eood’ (Bulgaria) was used. The particles had irregular shapes and sizes of 20–100 μm. The photos of several particles are shown in Figure 1.

Coffee in the ratio of 2 teaspoons (1 ml) per 100 ml of water was cooked in a cezve for 5 min and cooled to room temperature. With the help of a

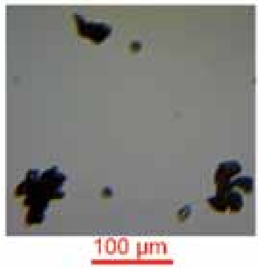

FIGURE 1
Photo of coffee particles.

FIGURE 2
Photo of electric discharge over a coffee drop (oblique view).

pipette the drops of coffee were deposited on aluminum foil with a thickness of 11 μm. Foil played the role of one of the electrodes.

Above the drop another electrode in the form of a stainless steel needle was fixed so that the gap between the top of the drop and the needle point was 2–3 mm wide. The pulse generator was connected to the electrodes. As a generator a household transformer type electric lighter, the model ‹Iskorka-6› (Russia) was used, which provided a sequence of high voltage nanosecond pulses (~15 kV). Pulses followed at a frequency of 20 Hz. When the load in the form of a spark gap was connected to the generator output, discharge current pulses appeared in the circuit.

Visualization of discharge was conducted using handheld digital microscope the model M44302, ‘Celestron’ (Chine). Photographs of dried droplets were made with a mobile phone camera, the model 1020, ‘Nokia-Lumia’ (Finland) equipped with optional lenses for macro shooting. Pictures of micro-fragments of drops were made with the help of a digital microscope, the model ‘Levenhuk’ D50L NG (Chine) equipped with a digital video camera D200. The photo of a single discharge is shown in Figure 2.

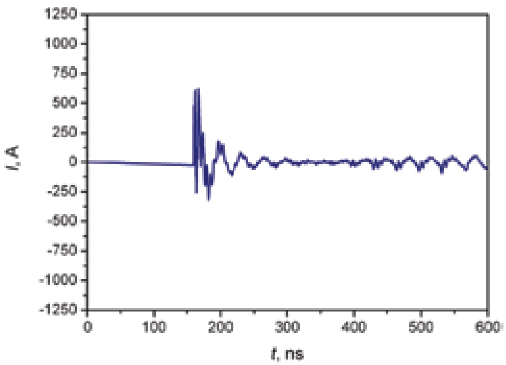

FIGURE 3
Oscillogram of the conduction current in the discharge.

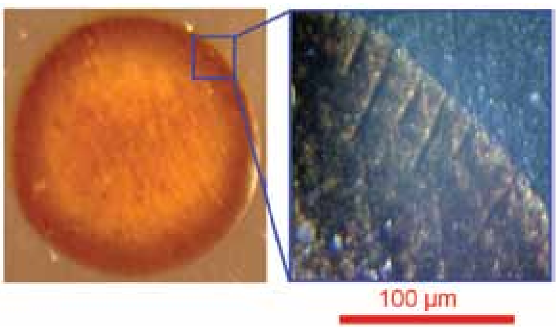

FIGURE 4
Photo of the dried control coffee drop not exposed to plasma (on the left) and its micro-fragment, which shows the formation of cracks (on the right).

A typical waveform of the conductive current impulse in the gap is shown in Figure 3. The method of obtaining this waveform from the recorded total current waveform has been described previously [14]. From Figure 3 it can be seen that during one pulse, current direction varies with a period of about 34 ns. It is the period of the oscillating circuit of the output circuit of the generator with a load. This current behavior is typical when the generator mismatches the load.

3 COFFEE STAIN PATTERNS WITHOUT DISCHARGES

Despite the extensive literature on the "coffee ring effect" there are no scientific works in which this effect was investigated on a metal substrate. Therefore, a series of control experiments to determine whether aluminum foil introduces any new features or not was conducted.

Figure 4 shows a typical coffee stain pattern on foil. The presented stain pattern shows that the foil use does not contribute to the appearance of new features. Thus, it may be concluded that the “coffee ring effect” is equally evident on both metal and dielectric substrates (compare the pattern on Figure 4 with patterns presented in [1,15−17]).

In addition, microscopic examination of the structure of the rings has shown that aluminum foil observed a radial cracks with the length of 20-50 μm, width of 5-7 μm, and an average distance from each other of about 25 μm, similar to those observed in other colloidal solutions [6,18−20]. It is noted in [20,21] that the distance λ between nearest cracks may be estimate in following manner: $\lambda \sim (B/\sigma rr)^{1/4} r^{1/2}$, where B is the bending modulus, r is the radial distance from the center of droplet, and σrr is the radial stress due to surface tension.

4 THE INFLUENCE OF DISCHARGES ON THE COFFEE STAIN PATTERNS

Exposure of a coffee drop to electric discharges was carried out in a periodic pulse mode, with pulse repetition frequency of 20 Hz from the moment the drop was applied on the foil until it was completely dry. As a result, the process of exposure took 5−10 min depending on the volume of the drop. Several tens of coffee drops were processed in this mode.

After drying the droplets visualization of coffee stains was made. It was found that the pattern of drop stain subjected to plasma discharges, was fundamentally different from the pattern of a dried control drop. The typical stain pattern of a treated droplet is shown in Figure 5.

Here, those particular patterns that emerged after plasma treatment of the drop are listed:

- plasma treated stain always has a central part that is similar in its form to a circle with a diameter of 200-500 μm, while the central part looks like a coating in the form of coffee beads with a diameter of 10−30 μm;
- stain which is located beyond the circle coincide with the initial drop boundary and may have internal concentric rings covering the central part of the circular;
- between the outer and inner rings arms are formed, often 6 or 8 pieces having the shape of arcs of flat spirals and the width of the arc of 30−100 μm;
- no cracking anywhere;
- coffee particles were distributed more evenly over the area of the stain. That is, the area occupied by the coffee particles in the stain is increased compared to the stain without discharges.

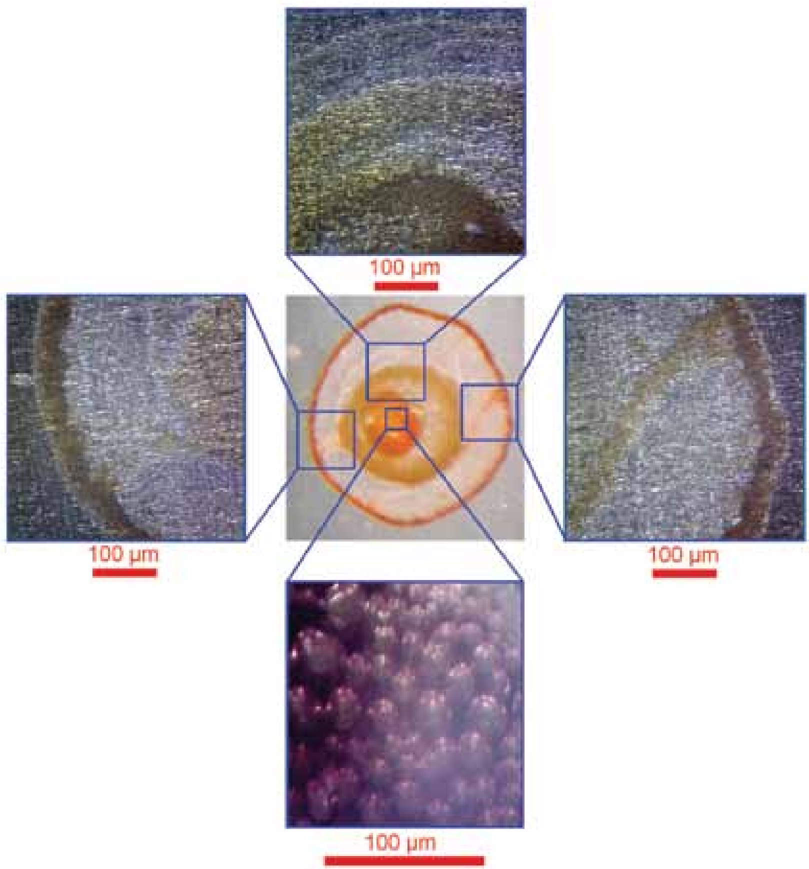

FIGURE 5
Photo of the dried control coffee drop exposed to plasma (in the center) and its micro-fragment (at the top, on the right, on the left – coffee spokes, at the bottom – central spot with spherical particles).

The analysis of these changes in patterns of stains makes it possible to assume that they occur due to two reasons: plasma of discharge induces wettability enhancement of foil [22] and electric discharges excite circular electrohydrodynamic flows in liquid [23,24].

The formation of a circular central part and inner rings on the spots of dried drops of colloids at the Marangoni convection was observed before [25,26]. The formation of arms was noticed here for the first time. It must be due to electrohydrodynamic circular flow of the liquid excited by the discharge. At the same time, the mechanism of arms formation is similar to the formation of mechanisms of a wavy surface shaping on a sandy bottom of the riverbed [27].

Coffee beads were also studied by pushing them with a thin needle. It was found that the balls have thin walls and there is gas inside. Each such bubble can be formed during electric breakdown in a viscous fluid [28,29].

5 CONCLUSIONS

In this paper, the effects of pulse-periodic sequence of nanosecond electric discharges on drying drops of coffee are examined. In the absence of discharges, the well-known “coffee ring effect” is observed. However, after the exposure to discharges the shape of the stain of dried droplets had another look and the structure in the form of concentric rings and spiral arms. The explanation of the observed effect is based on the mechanism of excitation of electrohydrodynamic circular flow under the influence of discharges. The fundamental significance of the work is to provide a new method of controlling of patterns of dried colloidal droplets by using nanosecond repetitively pulsed electric discharges affecting the top of the droplets. In particular, it turned out that the coffee particles were distributed more evenly over the area of the stain due to electrohydrodynamic flows that occur in the drop under the action of discharges. This effect can be used, for example, in inkjet printing.

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