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A Study of Paint Coat Characteristics Produced by Spray Paints from Shaken and Nonshaken Spray Cans

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ABSTRACT: The influence of shaking spray paint cans, prior to spraying, on the characteristics of the obtained paint coatings was studied. It was found that large variations in the characteristics of sprayed paint coatings can be obtained, depending on whether the cans were shaken before the spray was applied. Therefore, care should be taken in interpretation of the results obtained in comparison of paint when spray paints are involved. To account for the obtained results, the mechanism of spraying with unshaken spray cans was studied using both X-ray radiography of spray paints during spraying and simulated experiments with sand suspensions in water.

KEYWORDS: criminalistics, paints, spray paints, X-ray analysis

Characterization of spray paints may be necessary in investigating various types of criminal offenses. The typical construction of a spray paint can is shown in Fig. 1. According to the instructions written on spray paint cans, they should be shaken well before spraying in order to obtain good and reproducible results. If these instructions are not followed, variations may be expected in the characteristics of the obtained paint coatings. Such a problem was encountered by the authors while investigating a real case of an armed robbery.

To the best of our knowledge, this problem has not been dealt with before in the forensic science literature [*1*], although some problems of variations in color and energy-dispersive X-ray spectroscopy (EDS) spectra have been discussed [*2–4*].[2]

The purpose of this work was to study the variations between paint coatings obtained from unshaken and shaken spray paint cans, including the problem encountered in the real case. To account for the observed variations, we studied the mechanism of spraying unshaken spray paints using real-time X-ray radiography and simulated experiments with sand suspensions in water.

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FIG. 1—*An opened spray paint can, showing the location of the end of the plastic tube in close proximity to the bottom of the can.*

The Case

Two robbers escaped from the scene of the crime, riding a motorcycle. The motorcycle was later found abandoned, and it appeared to be stolen. Its vehicle identification number (VIN) plates had been changed and it had been repainted blue in order to mask its identity. The suspects were apprehended, and in their possession were found two spray cans of dark blue paint (New York Bronze Powder Company Inc., distributed in Israel by Tambur Ltd.). The laboratory was asked to compare the blue paint on the motorcycle with the blue spray paints.

Case Examination—Experimental Procedure

Chips of the blue paint on the motorcycle were taken, using a scalpel, and placed on a 1-in. (25.4-mm)-diameter aluminum stub coated with 3M No. 465 double-sided adhesive tape. The two cans of the blue spray paints were shaken well and the paint was sprayed on glass slides; it was allowed to dry, and then sample chips were taken and placed on the same stub.

Reflectance microspectrophotometry of the paint chips was carried out using the Docuspec TM/1 (Nanometrics Inc.) system, which is described elsewhere [*5,6*]. A ×20 objective was used to record spectra, and the measuring area was approximately 40 by 40 μm. Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) was carried out using a CamScan III scanning electron microscope combined with a Tracor Northern TN5400 EDS system. The operating conditions were as follows: the accelerating voltage was 25 kV; the beam current was about 1 nA; the live time was

100 s; the energy range/gain was 0 to 20 keV; the resolution was 10 eV/channel; and the analysis area was about 200 by 200 μm.

No difference was observed in the characteristics of the paint coatings obtained from the two blue spray paints. A small difference was found between the paint chips from the laboratory-produced coatings and those from the motorcycle in visible reflectance spectra. A considerable difference in the concentration of the inorganic material was found between the paint coating sampled from the motorcycle and the sample obtained from the well-shaken spray paint (Figs. 2 and 3, respectively), as expressed by the respective intensities of the X-ray continuum ("Bremsstrahlung"). Possible explanations for these results could be the following: either the paints were of different origins or the difference was associated with the painting process—that is, the difference in the extent to which the spray paint cans had been shaken prior to their use. To examine the latter

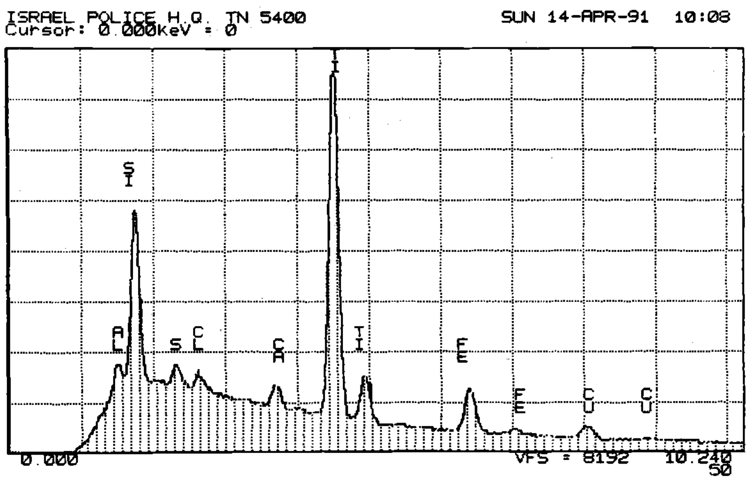

FIG. 2—*SEM/EDS spectrum of the blue paint sampled from the motorcycle.*

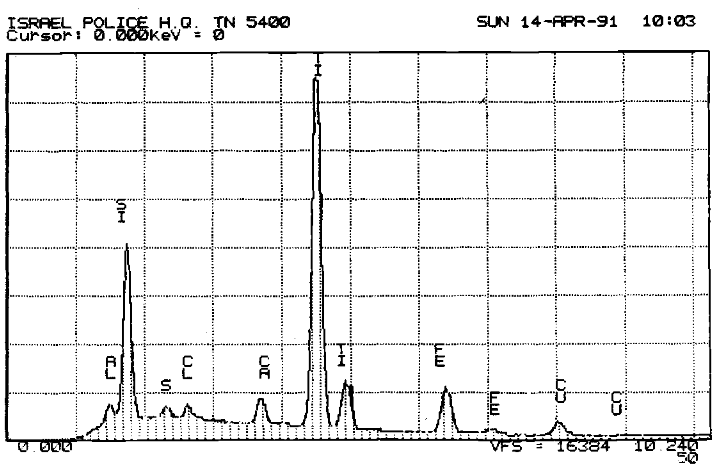

FIG. 3—*SEM/EDS spectrum of the blue paint coating obtained from a well-shaken blue spray paint can.*

possibility, the blue spray paint was applied without being shaken, after slight shaking, and after vigorous shaking. A match was obtained between the paint coating from the unshaken cans (Fig. 4) and the paint from the motorcycle (Fig. 2) in SEM/EDS spectra. On the other hand, the results obtained after slight shaking were quite similar to those obtained after vigorous shaking.

Experiments with Different Paint Sprays

Four additional spray paints were examined to study the effect of shaking or the lack of shaking on the characteristics of the obtained paint coating. All four spray paints were manufactured by the Illinois Bronze Paint Company, Lake Zurich, IL, and their colors were the following:

(*a*) gloss white 29357,
(*b*) all-purpose gray primer 363,
(*c*) gold 10064, and
(*d*) black 29358.

As in the case of the blue spray paints, three conditions of shaking were examined: no shaking, slight shaking, and vigorous shaking. In SEM/EDS spectra, results similar to those for the blue paints were obtained, except for the black paint. This exception was attributed to the low concentration of inorganic material in the black paint. For this reason, no additional experiments were carried out with the black spray paint.

Since transient phenomena were observed while spraying the unshaken spray paints, we decided to examine the paint coating characteristics of the spray of unshaken spray paints as a function of time. For this purpose, the following experiments were designed and carried out using the white, gray, and gold spray paints.

The spray cans were allowed to stay undisturbed for 24 h. Three persons were involved in the spraying experiment. One sprayed continuously; the second watched the time using a stopwatch and giving orders to the third person as to when to place a glass slide inside the spray stream and when to take it out of the stream. The slides were sprayed from a 30-cm distance, and the spraying duration for each experiment was 23 s. A glass slide

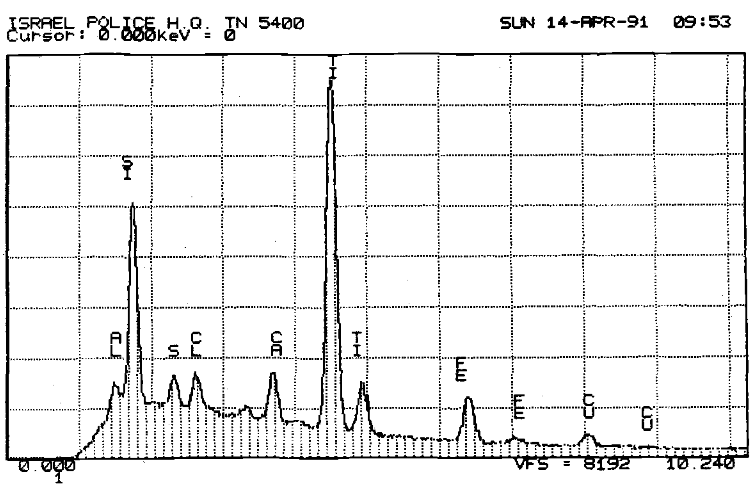

FIG. 4—*SEM/EDS spectrum of the paint coating obtained from an unshaken blue spray paint can.*

was sprayed for each of the following three time periods (within the above-mentioned 23-s spraying duration): 0 to 3 s, 10 to 13 s, and 20 to 23 s. After that, the spray cans were shaken well, operated for 3 s, and then a glass slide was placed inside the spray stream for 3 s. Therefore, for each of the spray paints we obtained four samples: three samples from the unshaken spray can and a fourth sample taken after shaking. The glass slides were then allowed to dry, and sample chips were taken according to the procedure mentioned above.

The SEM/EDS spectra of the obtained paint samples are shown in Figs. 5, 6, and 7. These figures show clearly the transient nature of the paint coating characteristics in the first seconds of spraying, when the spray cans had not been shaken. One can observe that, in the first phase of spraying, the concentration of the inorganic material in the coating is much higher than it is afterward, and it resembles the concentration obtained from the well-shaken can. This result is also clearly reflected in the appearance of the coatings: the coating from the first seconds of spraying of an unshaken can or a well-shaken one is much more opaque than the coatings obtained in the periods 10 to 13 s and 20 to 23 s. This difference in appearance was most pronounced in the case of the gray paint, where the coatings obtained from the well-shaken can and in the period 0 to 3 s were of a dark gray color, while the coatings obtained in the periods 10 to 13 s and 20 to 23 s resembled in color the coatings obtained from the white paint for the same periods of time. It is apparent that the SEM/EDS spectra of the coatings for the periods 10 to 13 s and 20 to 23 s are quite similar, which indicates that a steady state in spraying is obtained in this time range.

To account for the obtained results from a mechanistic point of view, X-ray radiographic experiments were designed and performed using the white, gray, and gold spray paints already described.

The radiographic system used was an RTVS/2530 real-time viewing system of Sector 6, Security Division of Camauto SA, B-1720 Dilbeec, Belgium. The system consisted of a battery-operated six-ray high pulse rate (HPR) model X-ray generator (operating conditions: 80 kV and 3 mA), a viewing unit with a high-performance fluoroscopic screen and camera, and a control and display unit equipped with a 9-in. (229-mm) monitor. The spray paint cans were placed at a distance of about 40 cm from the source.

We obtained hard copies of the X-ray radiograms in two ways:

1. A Sony video/graphic printer UP-850 was connected to the video output of the monitor.
2. Polaroid 57 (3000 ASA) 4- by 5-in. (102- by 127-mm) instant sheet film was attached behind the spray can, exposed for 20 to 30 s, and then developed in a Polaroid Land film holder.

Since photographs of much better quality were obtained with the Polaroid films, the first method was abandoned.

First, we wished to learn which part of the volume of the paint suspension is occupied by inorganic materials. The spray cans were radiographed at rest (Fig. 8) and after being shaken (Fig. 9). Since the tubes in the spray paint cans are made of a plastic material, it was impossible to visualize their placement in the paint suspensions by X-ray radiography. In order to observe their orientation and how close the tubes came to the bottom of the can, the spray cans were turned upside down and radiographed. Figure 10 shows that the tube practically reaches the bottom of the can, and therefore its end dips into the bulk of inorganic material in the unshaken state in the bottom of the spray paint can (compare Fig. 10 with Fig. 7*a*). This result was also confirmed by cutting open an empty spray paint can (Fig. 1).

We also examined the rate of settling of the inorganic material in the three paints studied. The spray paint cans were vigorously shaken and radiographed at intervals of 5

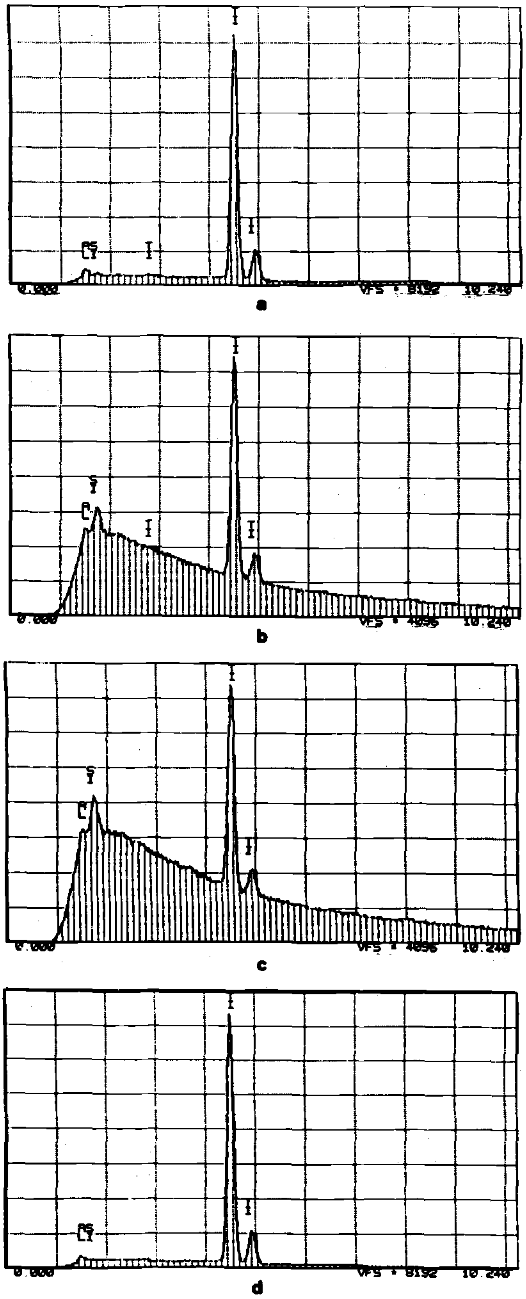

FIG. 5—*SEM/EDS spectra of white paint coatings sprayed for* (a) *0 to 3 s,* (b) *10 to 13 s, and* (c) *20 to 23 s and of* (d) *a well-shaken spray paint (see the text for details).*

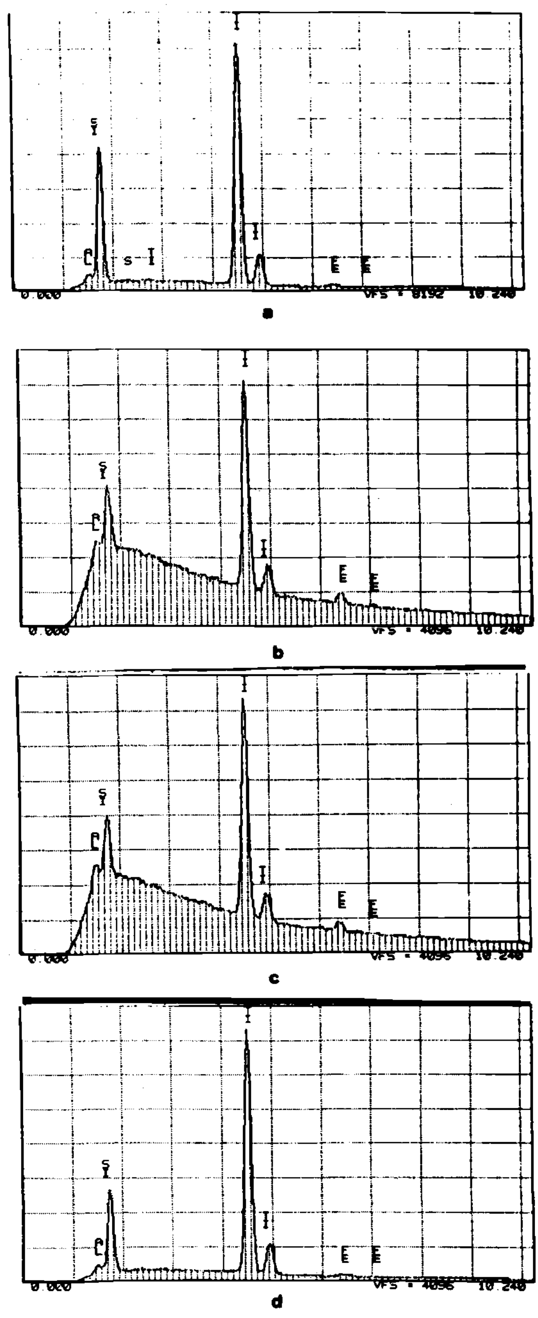

FIG. 6—*SEM/EDS spectra of the gray paint coatings (using the same experimental procedure described in Fig. 5).*

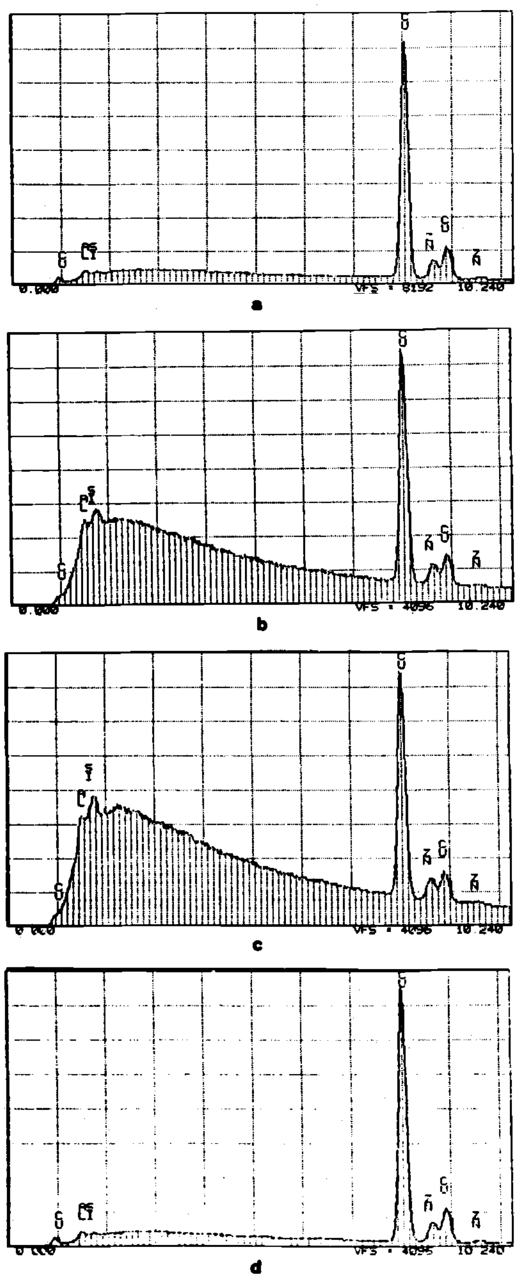

FIG. 7—*SEM/EDS spectra of the gold paint coatings (using the same experimental procedure described in Fig. 5).*

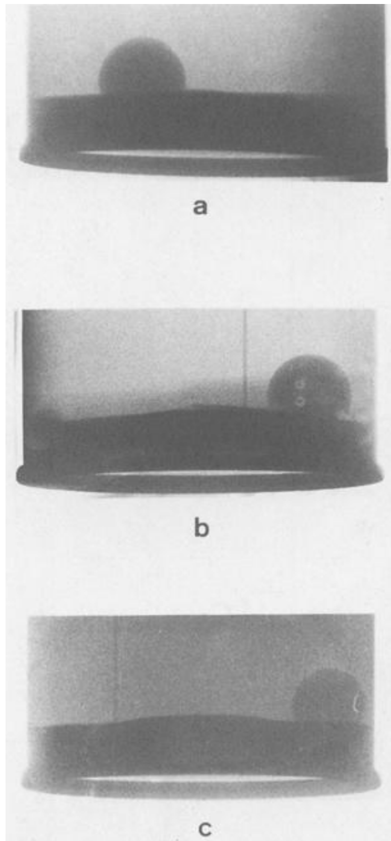

FIG. 8—*X-ray radiographs of the lower part of the spray paint cans in the three colors, at rest:* (a) *white,* (b) *gray, and* (c) *gold (the darker area is the layer of settled solids).*

min. It appeared that, in the gold paint, the settling was practically complete after 10 min. In the gray paint, the process was more complicated: after about 45 min, an interface plane was observed near the bottom of the can, where the density increased with time (Fig. 11). For the white paint, no settling was observed even 3 h after the can had been shaken.

In the final radiographic experiment, we wished to study what happens in the three spray paints during spraying. For this purpose, a special device, which operated the spray cans by remote control, was designed and constructed. Real-time X-ray radiography in these experiments was performed as follows. The X-ray system was turned on, followed by remote operation of the spray can. While being operated, the spray can was observed on the monitor for 20 to 30 s. This is the time needed for exposing the Polaroid 57 film.

In these experiments, we did not observe any disturbance in the settled solids in the three spray cans during spraying, and they apparently remained intact. It should be noted, however, that, in these radiographic experiments, the spray paint cans were radiographed perpendicular to their axes, and therefore not all the possible changes that could have occurred in the regions of the sediments could have been observed.

In our view, the only plausible mechanism for the observed results is the following. At the beginning of spraying unshaken spray paints, a high concentration of inorganic

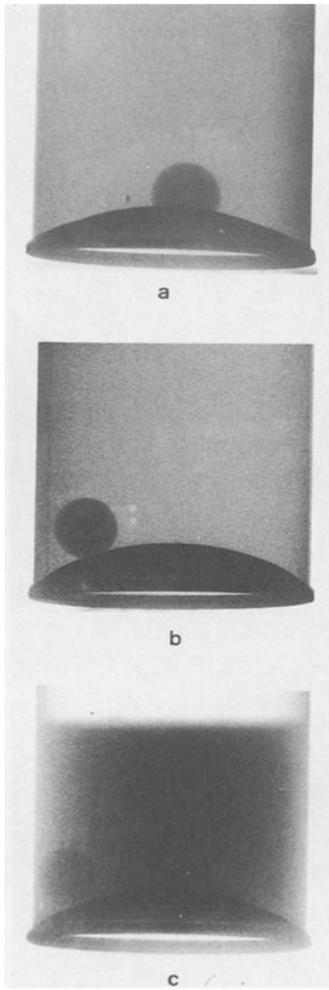

FIG. 9—*Radiographs of the lower part of the three spray paint cans when well shaken:* (a) *white,* (b) *gray, and* (c) *gold (the darker area is the convex shape of the can's bottom).*

material comes out first, since it is in the bottom of the can where the tube is located. Following that, the solvent above the settled solids "cleans itself a way" into the tube by creating a crater around the end of the tube so that, afterward, mostly solvent comes out during spraying.

Since we could not observe this phenomenon directly by X-ray radiography of the spray paint cans, we decided to carry out simulated experiments with sand suspensions in a glass trap vessel while viewing the process by transmitted visible light. The experimental setup is shown in Fig. 12. Building sand was used for preparing sand suspensions in water. In order to obtain suspensions that will settle down almost completely in a range of 1 to 2 h, considerable amounts of clay-particle-sized material were removed by mixing the sand in water and decanting the supernatant liquid after about 1 min of settling. This process was repeated several times and then the suspension was poured into the trap vessel. The height of the liquid was about 20 cm, the thickness of the settled solid

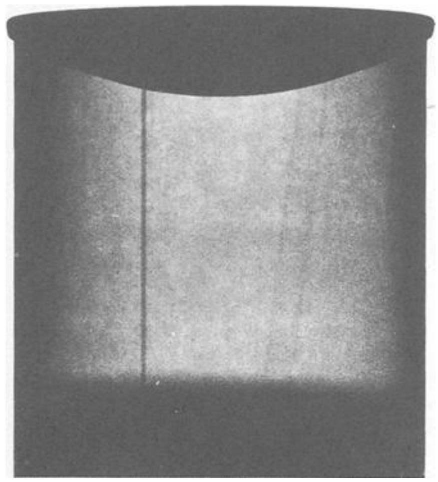

FIG. 10—*A radiograph of the lower part of the white spray paint can turned upside down. Notice that the tube reaches the bottom of the can.*

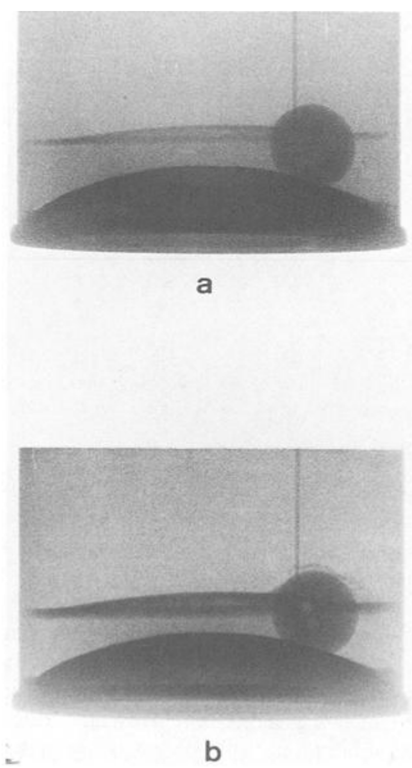

FIG. 11—*Radiographs of the lower part of the gray paint can at different times after vigorous shaking:* (a) *45 min after shaking,* (b) *2.5 h after shaking.*

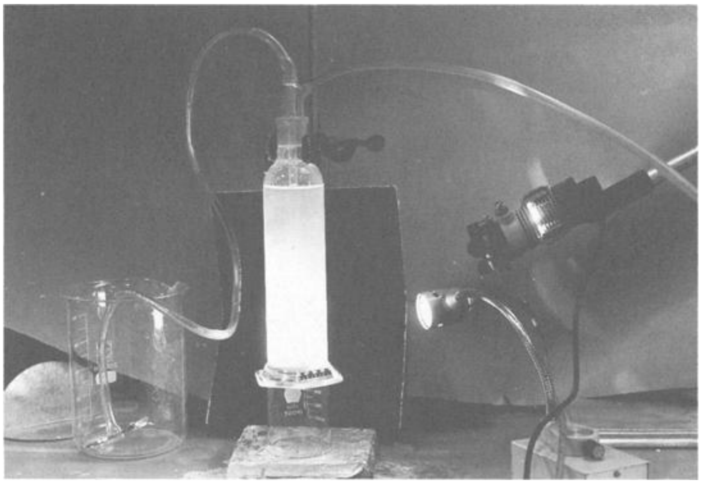

FIG. 12—*The experimental setup for spraying the sand suspensions.*

was about 1 cm, and the glass tube dipped into the sediment. The simulation of spraying was achieved by connecting the plastic tube at the right-hand side (Fig. 12) to a compressed air source and clamping the plastic tube at the left-hand side. Still photographs were taken during various steps of the spraying (Fig. 13) and the process was also video recorded by a video camera (Sanyo Top D5 VM-DSP). Hard copies from various steps of video recording were made using the Sony videographic printer mentioned earlier (Fig. 14).

It can be seen from Fig. 14 that, in the first few seconds, a dense material from the settled solid ascended the tube until a crater had been formed, which allowed a passage of almost clear liquid during the steady state.

Thus, our hypothesis concerning the mechanism of spraying of unshaken suspensions was proved, at least in the case of sand. It can be safely inferred that these phenomena also occur with spray paints. This conclusion is based on the results described previously concerning the characteristics of the paint coating and the X-ray radiography evidence.

Conclusions

We have shown that large variations are obtained in the characteristics of sprayed paint coatings, depending on whether or not the cans have been shaken prior to the spraying. Therefore, care should be taken in interpretation of the results obtained in comparison of paint when spray paints are involved.

Acknowledgment

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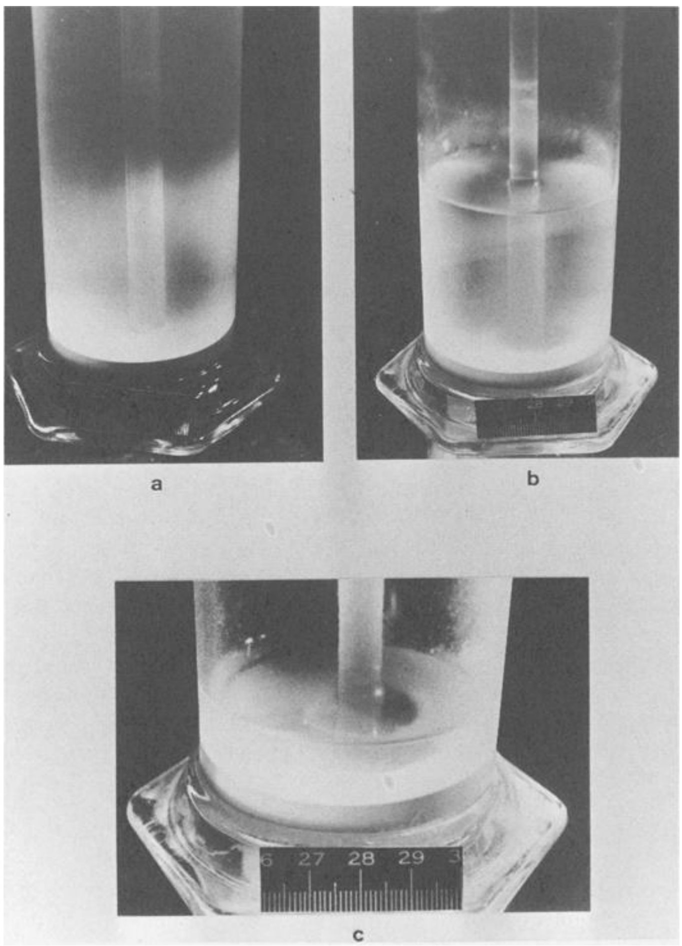

FIG. 13—*Still photographs taken during various steps of spraying the sand suspension:* (a) *the sand suspension after settling,* (b) *and* (c) *unshaken sand suspensions during spraying (notice the formation of the crater around the end of the tube).*

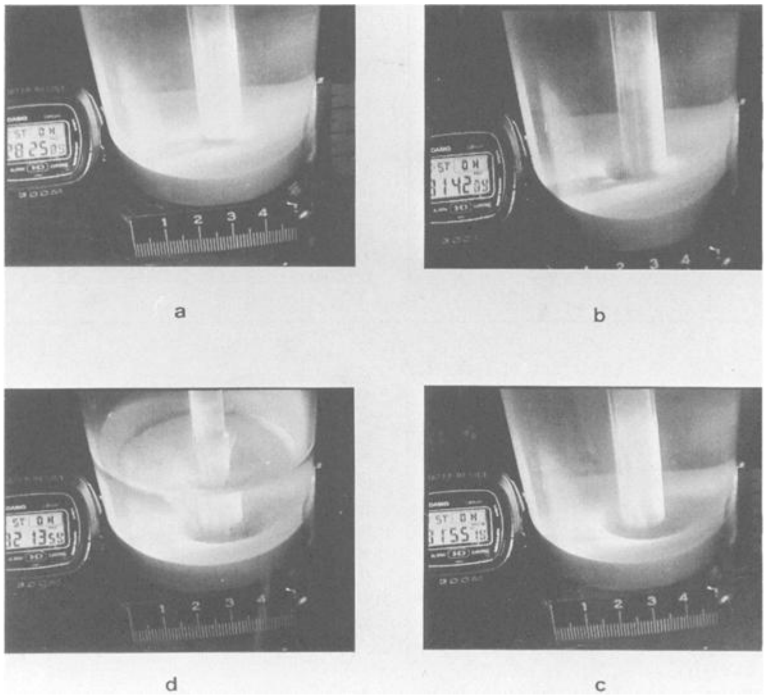

FIG. 14—*Hard copies of video recordings of various steps of spraying the sand suspension:* (a) *the sand suspension after settling,* (b) *the beginning of spraying (notice the plug of dense material ascending the tube),* (c) *13 s after* (b), (d) *30 s after* (b). *Notice that there was no significant change in the size of the crater from* (c) *to* (d).

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