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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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Preparation of Particles for Optical Studies

By

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ABSTRACT

The electroless nickel plating process for glass and divinylbenzene-styrene copolymer surfaces was developed from the individual conditioning, sensitizing, activation, and plating steps. The optimum conditions for the chemical plating of nickel on 1 mm, 0.100 mm, and 0.050 mm glass particles and divinylbenzene-styrene copolymer particles in the size range of 0.250 mm to 0.425 mm were determined. The thickness of nickel deposit on 1 mm glass particles and the change in their average terminal velocity in water due to nickel deposits were measured.

ACKNOWLEDGEMENTS

I wish to express my appreciation to Dr. T.J. Hanratty for his guidance through the course of this project.

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INTRODUCTION

Successful application of photography in fluid mechanics studies requires the use of small particles to monitor the behavior of the fluid. Ideal particles for this purpose would have density equal to the density of the fluid and a smooth, reflective surface for clear images. Use of glass and polymer particles produces good results, but the size of the spheres is limited to about 0.100 mm due to inadequate reflection of light at smaller sizes. Chemical plating of glass and polymer with nickel was proposed as a way of improving the reflection of light from particles' surface without a significant change in density.

LITERATURE REVIEW

The chemical plating of nonmetallic materials like plastics, ceramics, and glass has been developed, during the past century, into a process consisting of a number of steps which prepare the material's surface and coat it with a metal. Although there may be some variations in the steps, generally the whole process consists of the following: etching, sensitizing, nucleation, and electroless plating.[1] For some plastics with hydrophobic surfaces, the process is preceded by an additional treatment of the plastic with a solvent to make its surface hydrophilic.[2]

The solvent treatment of plastics before etching is variable. Some plastics that require this step are polystyrene, polyethylene, polyvinylchloride, polysulfone, and Teflon. The solvent chosen should make the surface hydrophilic without degrading it. The solvent must be carefully removed by ample rinsing with water.[3]

Conditioning

The etching, or conditioning, may be carried out by chemical or mechanical means. This stage in the plating process determines the adhesion of the metal since it roughens the surface of the material to be plated. The chemical method usually involves the use of a chromic-sulfuric acid solution. Generally, the solution is near its saturation point with chromic acid, and the treatment lasts anywhere from 2 to 30 minutes at temperatures varying from room temperature to 160 °F depending on the material.[4] The mechanical methods that may be utilized to accomplish the same results are tumbling and blasting.[5]

Chemical conditioning, however, has advantages over mechanical methods. Use of chemical etchants is easier to carry out, more economical, and produces higher bond strengths. Disadvantages of chemical conditioning are degradation of polymer properties due to polymer-solvent interaction.[6]

Sensitizing

The sensitizing step which follows etching is critical for chemical bonding. The material surface is coated with a layer of Sn(II) by immersing it in stannous chloride solution for 1 to 2 minutes at room temperature and rinsing it with deionized water.[7] Precautions must be taken to prevent photo-oxidation of Sn(II) to Sn(IV) by ultraviolet radiation. The immersion of particles in the solution results in tin deposits of approximately a microgram/cm^2.[8] The depositing of Sn(II) on the surface proceeds by a mechanism of colloid formation in solution due to air oxidation and hydrolysis of Sn(II). Precipitation of tin on the surface occurs as a result of an increase in pH during rinsing with deionized water.[9] Factors like pH, concentration of stannous chloride, age of the solution, as well as substrate preparation and procedure used for the sensitizing step, influence the chemical and structural characteristics of the Sn(II) deposit.[10]

Activation

The activation step in chemical plating is crucial for the depositing of metal. A variety of metals such as palladium, gold, silver, and platinum, have been used as activators. However, the most frequently utilized catalyst is an aqueous solution of palladium chloride which is acidic due to the hydrochloric acid used to dissolve the crystals.[11] The palladium ions in the solution are chemically reduced to a metal according to the following reaction:

$$Sn(II) + Pd(II) \text{------>} Sn(IV) + Pd^\circ$$

The palladium metal deposits on the surface of the previously sensitized material and acts as a catalyst for nickel coating. In the areas where Sn(II), precipitated on the material's surface, was reduced to Sn(IV) prior to the activation step, plating does not occur.[12]

A number of factors like pH of the solution, concentration of palladium, temperature, and immersion time influence the effectiveness of palladium as a catalyst.[13] It was found that the pH of approximately 4.1 to 4.8 gave best results.[14] However, as the temperature increased, a wider pH range could be used. The increase in concentration of palladium also resulted in better catalyst coverage of the surface to be plated and a wider pH range acceptable for solution.[15] Combination of pH, temperature, and palladium concentration should be considered for optimum operating conditions.

Plating

A number of bath compositions for the electroless plating of nickel have been developed since 1946 when Brenner and Riddell of the National Bureau of Standards published a paper describing the conditions for selective deposition of nickel from aqueous solution.[16] The basic components of the plating bath are nickel salt, a hypophosphite ion serving as a reducing agent, and a salt acting as a buffer and a complexing agent for the nickel.[17] The deposit consists of 85 to 97 percent nickel and 3 to 15 percent phosphorus.[18]

The autocatalytic reactions taking place in the solution are believed to be:

$$(H_2PO_2)^- + H_2O \xrightarrow{\text{catalytic Ni}^\circ} H^+ + (HPO_3)^{2-} + 2H\ (\text{catalytic})$$

$$Ni^{2+} + 2H\ (\text{catalytic}) \dashrightarrow Ni^\circ + 2H^+$$

$$(H_2PO_2)^- + H\ (\text{catalytic}) \dashrightarrow H_2O + OH^- + P$$

$$(H_2PO_2)^- + H_2O \xrightarrow{\text{catalytic Ni}^\circ} H^+ + (HPO_3)^{2-} + H_2$$

where 2H (catalytic) stands for hydrogen atoms loosely bonded to Ni°.[19] Originally, palladium metal provides the catalytic surface for plating.

As can be seen from the equations, hypophosphite anions are dehydrogenated by the catalytic surface of palladium or nickel to form acid orthophosphite anions. The nickel ions in turn are reduced to metal by the adsorbed hydrogen atoms.[20] Deposition of nickel metal and oxidation of hypophosphite occur as separate steps and do not have to take place on the same surface.[21] Reduction of the hypophosphite anions by the adsorbed hydrogen occurs parallel to the above mentioned reactions, and it results in phosphorus, water, and hydroxyl ions.[22] The oxidation of hypophosphite anions resulting in acid orthophosphite anion and gaseous hydrogen is independent of the other three reactions, and it results in a decrease in the utilization of hypophosphite for reducing nickel cations to about 33%.[23]

The rate of depositing and stability of the plating bath are two major considerations in determining the composition of the solution. The rate of nickel plating is proportional to temperature, hypophosphite concentration, and pH range. On the other hand, the stability of the bath increases as these three factors decrease.[24]

"The rate of deposition is an exponential function of temperature."[25] However, when temperatures close to the boiling point of the solution are used, the stability of the bath decreases. Increasing the temperature of the plating bath results in a higher deposition rate, higher hydrogen evolution, and greater probability of decomposition.[26]

Hypophosphite concentration is directly proportional to the rate of plating. The mechanisms for the reactions responsible for nickel coating are dependent on the concentration of hypophosphite.[27] As the concentration of hypophosphite increases, the stability of the plating bath decreases due to the bulk reduction of the nickel ions rather than the catalytic plating on the desired surface.[28] According to Gutzeit and Krieg, the optimum conditions for nickel plating are as follows: concentration of hypophosphite ion within the range of 0.15 to 0.35 M with 0.22 to 0.23 M being preferred, and ratio of molar concentrations of Ni^{2+} to $(H_2PO_2)^-$ within 0.25 to 0.60 range with 0.3 to 0.45 being most beneficial.[29]

Hydrogen ion concentration in the plating solution is another determining factor in the deposition rate. Most baths operate in the acidic range; however, alkaline solutions were also developed. For acidic solutions, the range of pH desirable for plating is 3 to 7. Overall, the rate of deposition increases with an increase in pH in that range.[30] Plating below pH of 3 proceeds very slowly, and above pH 7 oxidation of hypophosphite begins to occur mainly by the following reaction:

$$(H_2PO_2)^- + OH^- \text{------->} (HPO_3)^- + H_2 .$$[31]

Decreasing hydrogen ion concentration in the solution gives the following results: higher depositing rate, lower solubility of nickel phosphite, lower phosphorous content, and increased probability of decomposition due to change from catalytic to homogeneous reaction of the hypophosphite.[32]

Alkaline baths, although less frequently used than acidic baths are easier to control. Keeping the pH of the solution within the limit for good plating results is not a problem. Precipitation of nickel phosphite is also alleviated in the basic solution.[33]

To prevent rapid changes in pH, buffers are added to the plating solution. They also act as complexing agents for nickel ions.[34] By chelating nickel ions, formation of nickel orthophosphite, which has a solubility of about 0.05 M to 0.07 M under plating conditions, is reduced thus preventing its precipitation and bath decomposition.[35] The disadvantage of using the complexing agents is that they somewhat retard the plating rate.[36] Additives like stabilizers acting as inhibitors and exaltants producing higher plating rates are used in some baths to give best results.

Electroless nickel deposits have characteristics that make the plating process desirable. Since electroless nickel is an alloy of nickel and phosphorus, its deposits are harder, more corrosion resistant, and less magnetic than those of electrolytic nickel.[37] Electroless nickel also results in more uniform coating, abscence of porosity, and homogeneous structure without crystal boundaries as compared to electrolytic nickel.[38] Adhesion to nonmetallic materials is dependent on adsorption bonds and is reported to be 3 to 10 lb/in.[39] Overall, electroless nickel plating is a favorable process for nonmetallic materials.

EXPERIMENTAL

The general plating procedure was used for coating of glass beads with diameter of 1 mm, 0.100 mm, and 0.050 mm as well as a mixture of divinylbenzene-styrene copolymer beads ranging in size from 0.250 mm to 0.425 mm. The etching solution consisted of 7.5 g. $K_2Cr_2O_7$, 12 mL concentrated H_2SO_4, and 25 mL deionized water.[36] Potassium dichromate was poured into a flask containing water. Sulfuric acid was slowly added to the flask, and the mixture was swirled after each addition to ensure uniform composition. The solution was allowed to cool down to room temperature. When the room temperature was reached, the conditioning solution was transferred into a beaker containing particles and a magnetic stirring bar. The magnetic stirrer was turned on as soon as the solution was poured into the beaker. The particles remained in the conditioning solution for one to two minutes. At that time the solution was diluted with water, and it was vacuum filtered into a flask. The particles were rinsed with deionized water to make sure that the yellow etching solution was removed.

The sensitizing solution was composed of 7 g. stannous chloride, 21 mL concentrated hydrochloric acid and 79 mL deionized water.[37] The solution, stored in a flask, was poured into a beaker containing etched particles. The sensitizing solution with particles was kept well mixed using the magnetic stirrer. The step lasted for 1 to 2 minutes at room temperature. The solution was vacuum filtered, and the particles were rinsed with deionized water.

The activating solution contained 0.0200 g. $PdCl_2$ which was first dissolved in 1 mL concentrated HCl, and then 50 mL of 0.1 M NaOH and 49 mL deionized water were added [3]. The solution was placed in 50°C water bath until it reached thermal equilibrium. The particles were submerged in the stirred solution for 1 to 4 minutes. Afterwards, the particles were vacuum filtered, rinsed with deionized water, and allowed to dry.

The plating solution was comprised of 1.5 g. nickel chloride, 2.30 g. sodium glycolate, 0.80 g. glycine, 2.5 g. sodium hypophosphite, 3.0 g. sodium carbonate, and 100 mL deionized water.[39] When all the compounds were dissolved in the solution at room temperature, plating was carried out by pouring the solution into a beaker with dry activated particles. The particles remained in the solution for 3 to 10 minutes while the solution was slowly stirred with the magnetic bar stirrer. The time necessary for plating depended on the size of the particles and the thickness of deposit required. When the desired thickness was achieved, the particles were vacuum filtered from the solution and washed with deionized water.

Additional steps were carried out for plating 0.050 mm glass spheres and divinylbenzene-styrene particles. Divinylbenzene-styrene copolymer beads were treated with the concentrated nitric acid for 2 to 4 minute periods to prepare the surface for the plating process. Glass particles with the diameter of 0.050 mm were sifted before and after plating to ensure that they are within the range of 0.053 to 0.045 mm.

Testing of the thickness of nickel deposits on 1 mm glass particles was carried out. Plated 1 mm glass beads were mixed with Quick Stick G-C Electronics epoxy glue, and the sample was left overnight to harden. The formed pellet was polished using sand paper on a Buehler Ltd. Apparatus for Microstructural Analysis. Polishing exposed the cross-sectional areas of the particles, the particles were colored with a red pen, and the nickel coating thickness was measured under magnification of 50 times.

The effect of nickel plating on the density of the 1 mm glass particles was observed by determining their mass and the average terminal velocities in water before and after plating. An analytical balance with the precision of 0.001 g. was used to determine mass changes. The average terminal velocity of 50 1 mm glass particles in water was measured in a 1000 mL graduated cylinder using a stopwatch with a precision to 0.01 second.

Adhesion of nickel deposits to glass and polymer surfaces was assessed qualitatively by placing coated 1 mm glass particles and divinylbenzene-styrene copolymer particles on masking tape. After removing the particles, the tape was checked for any remains of nickel. Brightness of nickel deposits was verified by visual examination.

RESULTS

The process of electroless nickel plating on non-metallic surfaces was examined. Experiments with the chemical nickel coating on glass and divinylbenzene-styrene copolymer beads were carried out. Tests to determine optimum conditions for the process plating rate, adhesion of nickel to non-metallic surfaces, and density changes in the particles were conducted.

The basic steps for the process of electroless nickel plating were chosen as etching, sensitizing, activating, and low temperature plating. The etching solution, which was saturated in chromic-sulfuric acid, cleaned and roughened the particle's surface. The sensitizing solution covered the surface of the particles with Sn (II) preparing them for the activating step with palladium chloride. The most efficient conditions for the activating step were determined to be 2 to 4 minute immersion time, temperature of 50°C, pH of 1.17, and the concentration of 0.00113 M to 0.00244 M $PdCl_2$. A low temperature bath was chosen as the plating solution to prevent melting of the substrate surfaces.

Nickel chloride ($NiCl_2 \cdot 6H_2O$) was used as a source of the nickel cation with sodium hypophosphite serving as the reducing agent. Sodium carbonate was utilized as a buffer to maintain the pH of the bath solution at approximately 8. Glycine and sodium glycolate acted as complexing agents for Ni^{2+}. The concentration of hypophosphite in the plating solution was approximately 0.284 M which is within the preferred range of 0.15 to 0.35 M.[40] The molar ratio of Ni^{2+} to $(H_2PO_2)^-$ was 0.22 which was also determined to be beneficial.[41] As plating proceeded, the bath solution changed from deep blue to light blue color with a grey undertone. The entire process of nickel coating was carried out without long interruptions between steps for good plating results.

Several experiments were performed on 1 mm glass particles (Fig. 1). The etching and sensitizing steps were carried out for 1 and 2 minute intervals. Even though the immersion time in etching and sensitizing solutions did not have a considerable effect on the plating

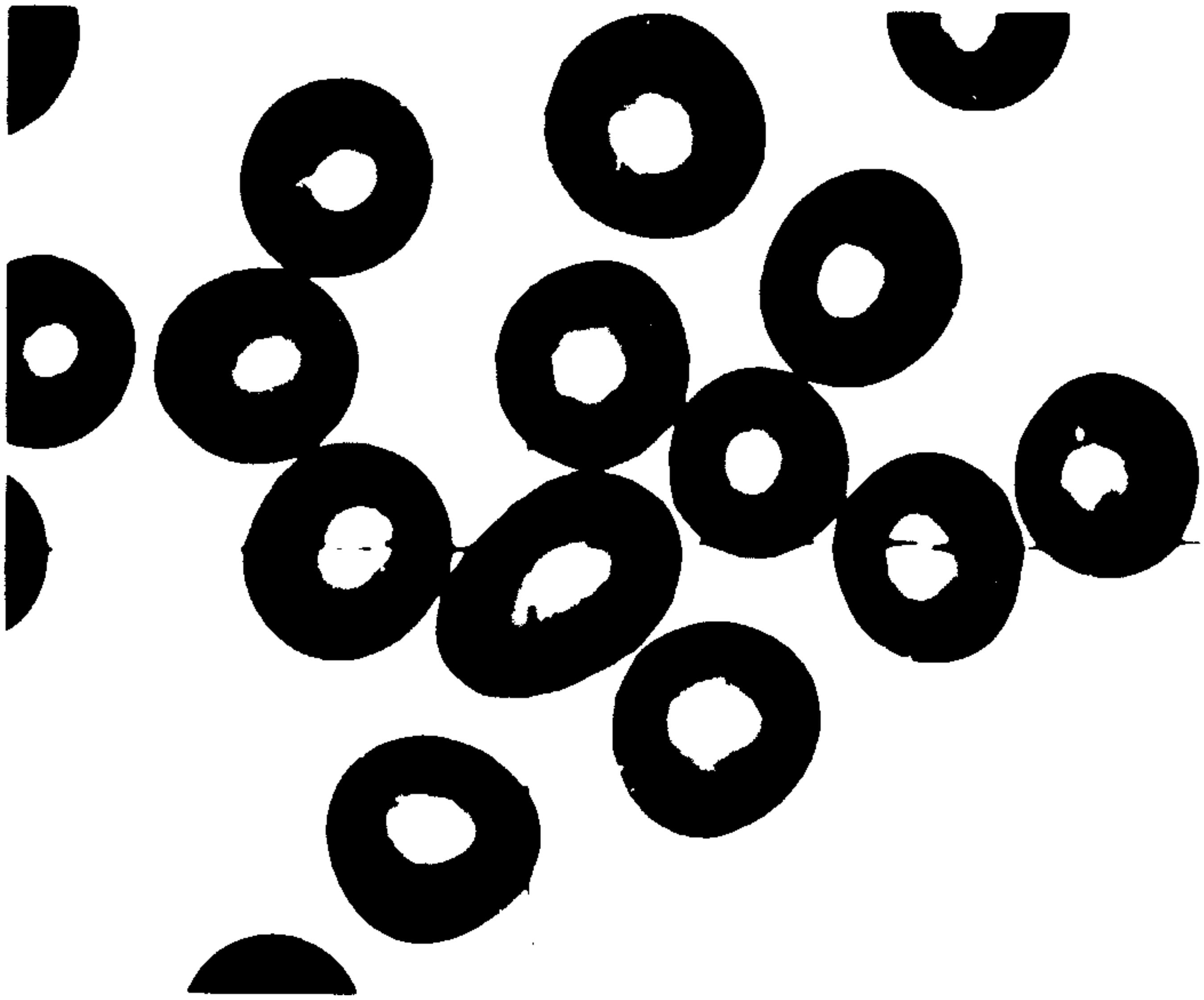

Figure 1.

1 mm Glass Particles Magnified 23 Times.

of nickel on glass beads, 2 minute periods for conditioning and sensitizing were preferred. In the activating stage, a variety of conditions were utilized to obtain the best deposits of nickel. The immersion time was increased from 1 to 2 minutes. PH of the solution was increased from -0.901 to 1.17 since at negative pH plating did not occur. The temperature of the activating solution was raised from room temperature to 50°C to ensure better coverage of the glass surface. Plating of particles was carried out for periods of time ranging from 3 to 10 minutes; however, the optimum time interval required for good nickel deposition was 5 minutes (Fig. 2). Allowing the particles to remain in the plating bath for 3 to 4 minutes did not result in complete coverage of all glass beads (Fig. 3). Plating for longer than 5 minutes did not produce any significant improvement in the nickel deposition.

A variety of tests was performed to check the thickness of the nickel coating, changes in the density of the plated particles, adhesion of the nickel to the glass surface, and appearance of the nickel deposit.

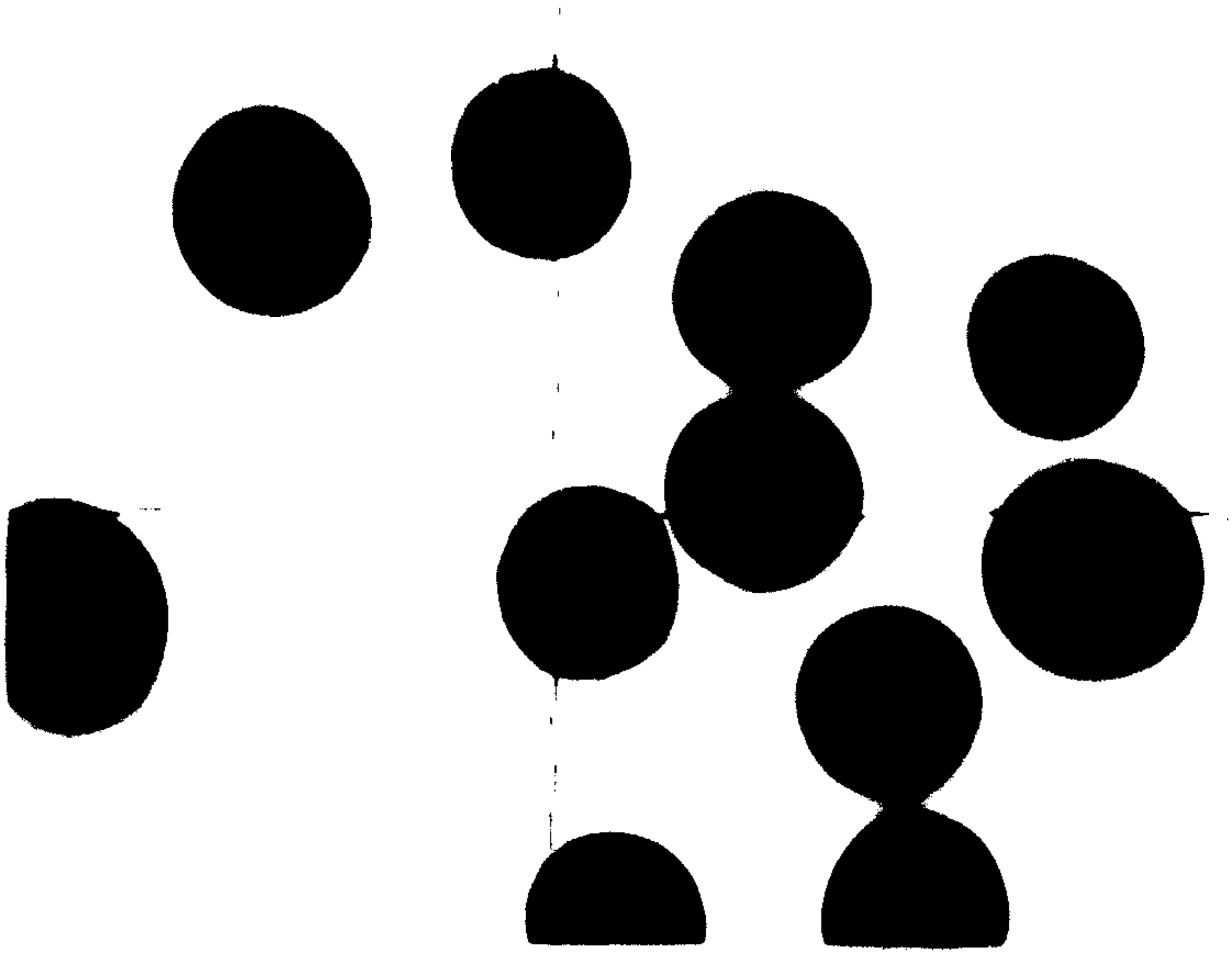

Figure 2.

1 mm Glass Particles Plated For 5 Minutes Under Optimum Conditions

Magnified 23 Times.

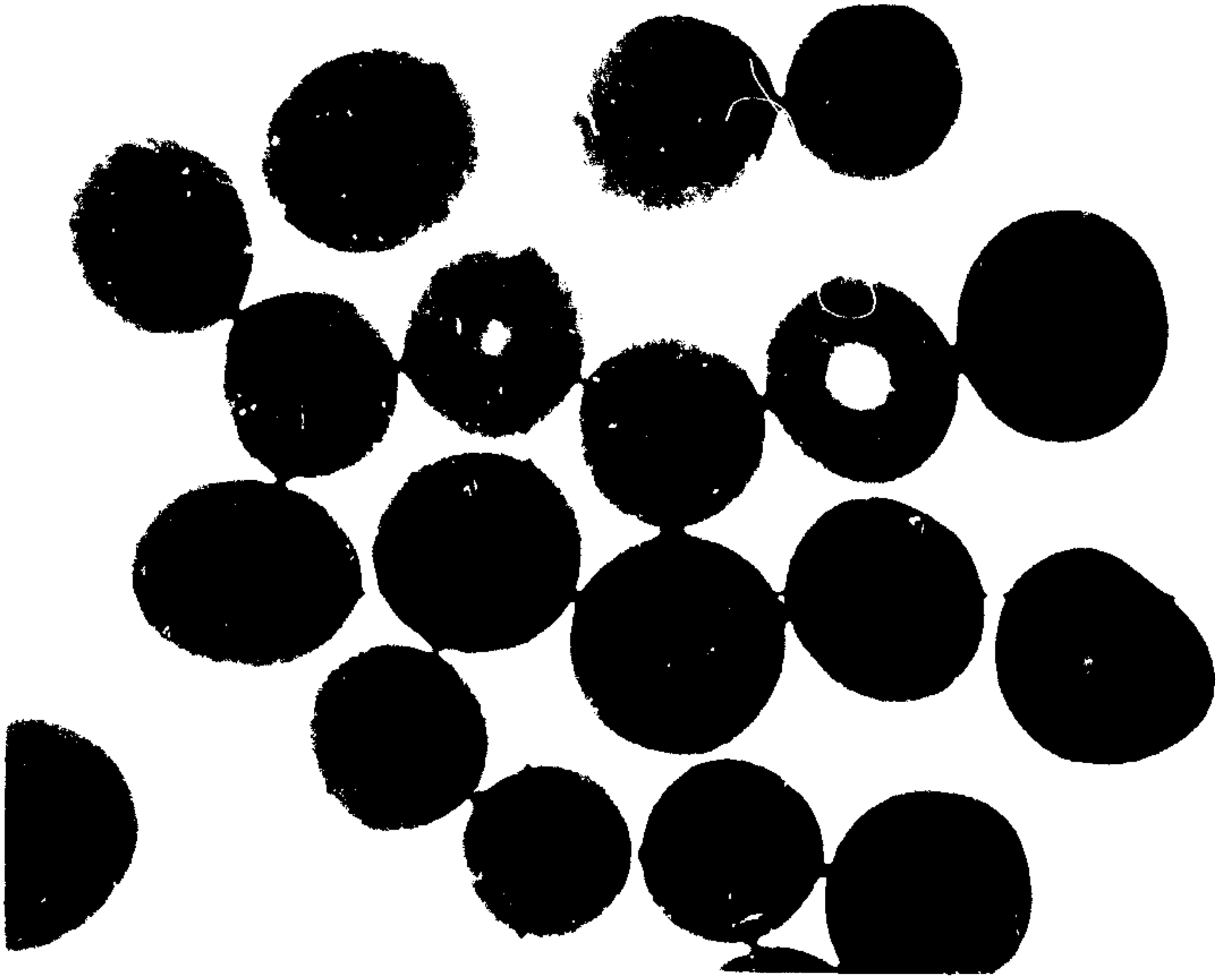

Figure 3.

1 mm Glass Particles Plated For 4 Minutes Under Optimum Conditions

Magnified 23 Times.

Thickness of the nickel coating was measured in cross sections of 1 mm nickel coated particles placed in epoxy glue. The average thickness of the nickel deposit for 1 mm glass beads plated for 5 minutes at optimum conditions was measured to be 0.020 ± 0.004 mm making the plating rate equal to 0.004 ± 0.001 mm/min. In two nickel plating experiments the mass of 50 1 mm glass beads was checked before and after plating occurred. The mass of the two samples of 50 spheres remained constant at 0.0834 g. and 0.1277 g. throughout the course of the experiment according to the analytical balance precise to 0.0001 g. The difference in mass of the two samples was due to variation in size of the particles.

In the same experiment changes in the average terminal velocities of 1 mm glass particles in water were measured (Table 1). In both cases average terminal velocities increased by 0.018 m/s after plating indicating an increase of 10.2% and 9.3%. There was no significant increase in the density of the particles due to nickel deposit.

Table 1.

Average Terminal Velocities of 1 mm Glass Particles in Water.

Before Plating		After Plating	
Time (sec.)	Velocity (m/sec.)	Time (sec.)	Velocity (m/sec.)
1.81 ± 0.16	0.177 ± 0.016	1.76 ± 0.14	0.182 ± 0.014
1.65 ± 0.13	0.194 ± 0.015	1.60 ± 0.10	0.200 ± 0.013

Testing the adhesion of nickel deposits to glass surface using masking tape produced very good results. There were no visible signs of nickel remaining on the tape. Overall, plating of 1 mm glass particles at the optimum conditions described gives smooth, bright, even deposits.

For 0.100 mm glass particles (Fig. 4) , similar plating conditions were chosen as for 1 mm glass beads. Etching, sensitizing, and activating steps were carried out for 2 minutes each. At 50°C the activating solution had a pH of 1.17 and a concentration of $PdCl_2$ equal to 0.00122 M. Plating continued for 3 minutes. Bright, even deposits were obtained.

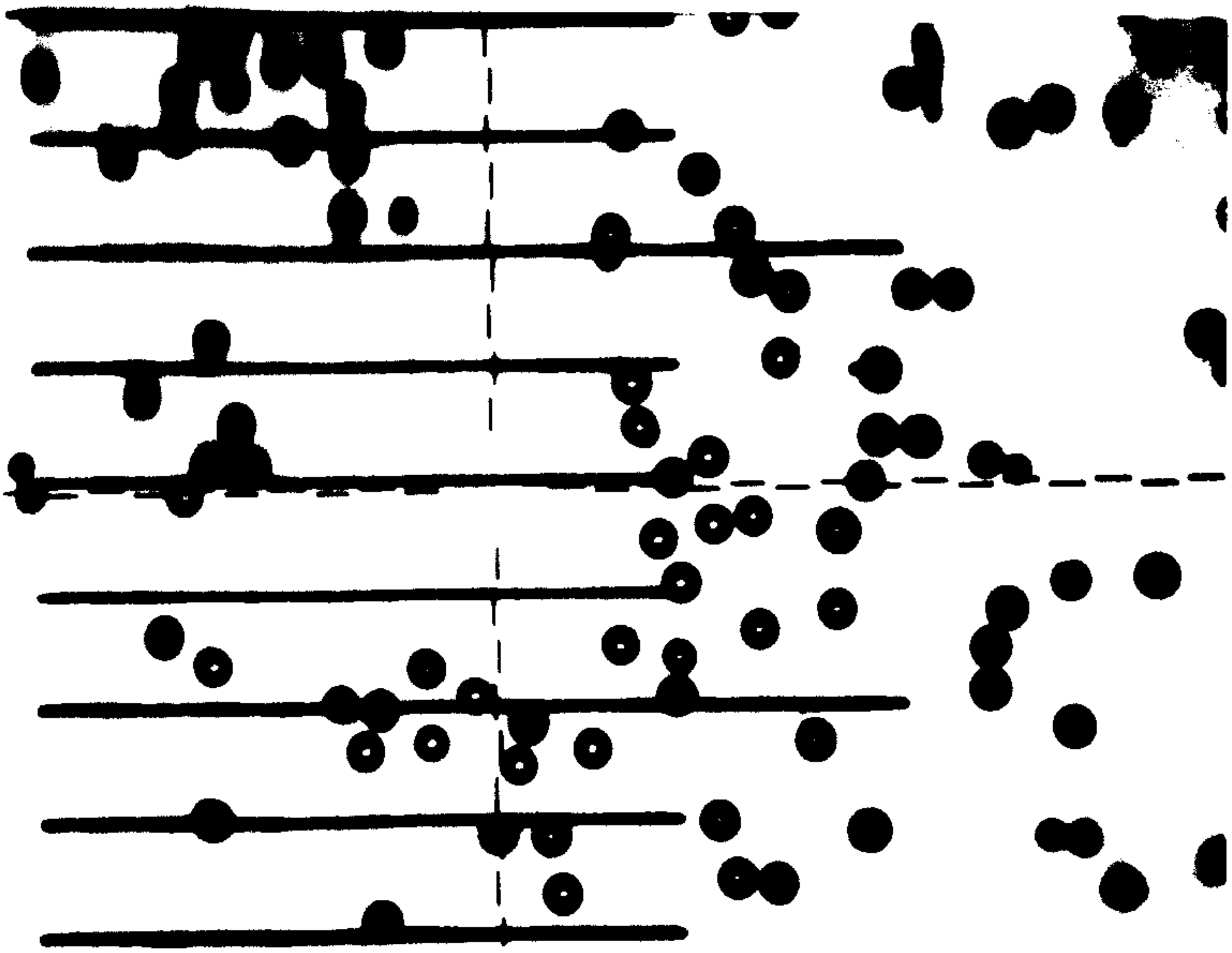

Figure 4.

0.100 mm Glass Particles Magnified 56 Times.

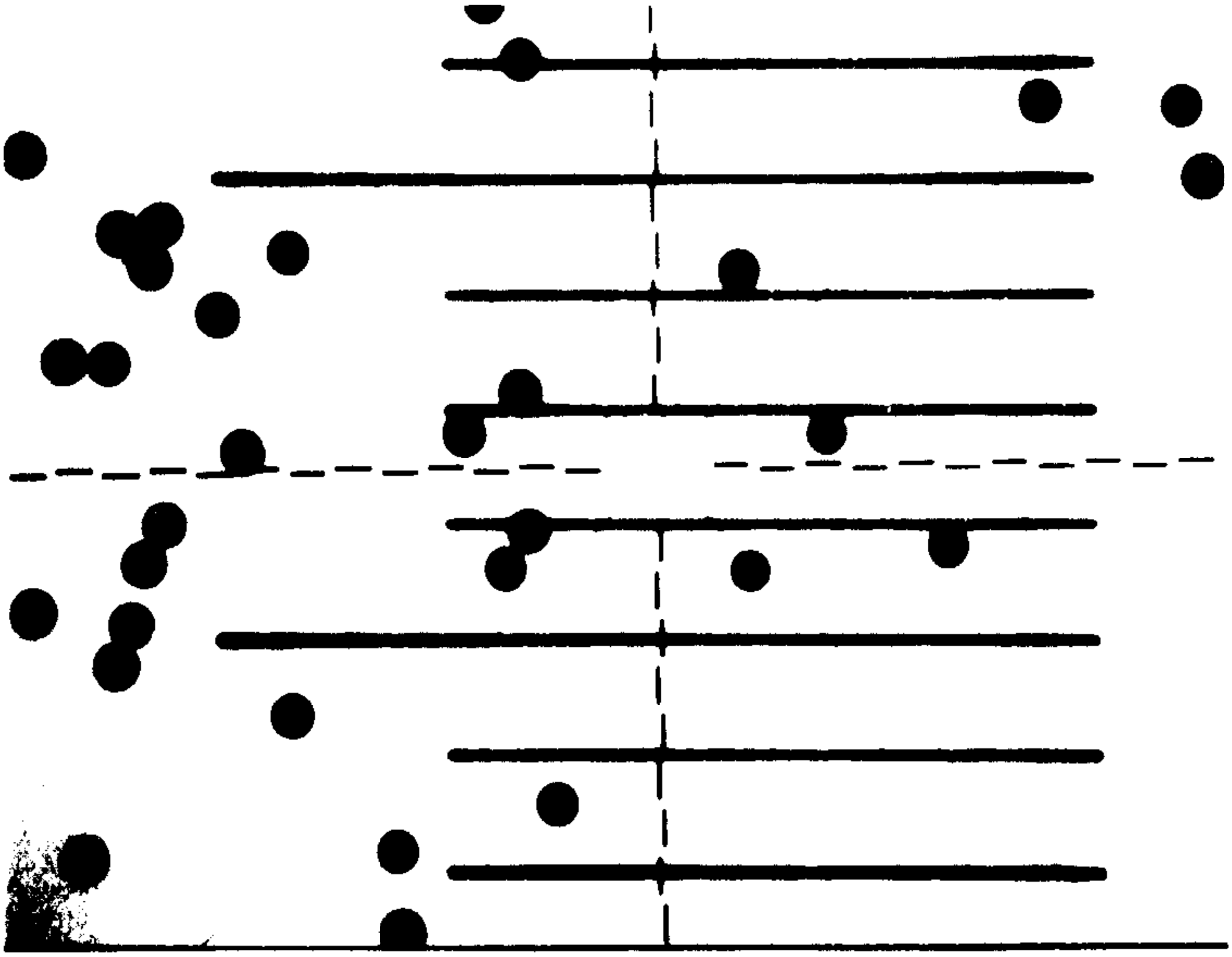

Figure 5.

0.100 mm Plated Particles Magnified 56 Times.

Several attempts at plating 0.050 mm glass beads were made (Fig. 6). The main problem encountered was uneven coating of particles caused by the surface tension. The problem was minimized by using higher stirring rates on the magnetic stirrer and changing the conditions of the activating step. Results of two different experiments are presented in Figures 7 and 8. In both cases 2 minute immersion time was employed for etching and sensitizing. For the particles in Figure 7, the activating step conditions were pH of 0.873, 0.00126 M $PdCl_2$, temperature of 50^oC, and 3 minute immersion time. Plating began at approximately 300 seconds after placing the particles in the bath solution and lasted for 180 seconds. Considerable number of particles remained unplated. Particles represented in Figure 8 were placed in the activating solution at 60^oC, pH of 1.17, and 0.00100 M $PdCl_2$ for 4 minutes. Immersion of particles in the plating bath proceeded for total of 500 seconds although onset of coating was noticed at approximately 300 seconds. Definite improvement in the coating of particles was observed even though small number of beads still remained unplated.

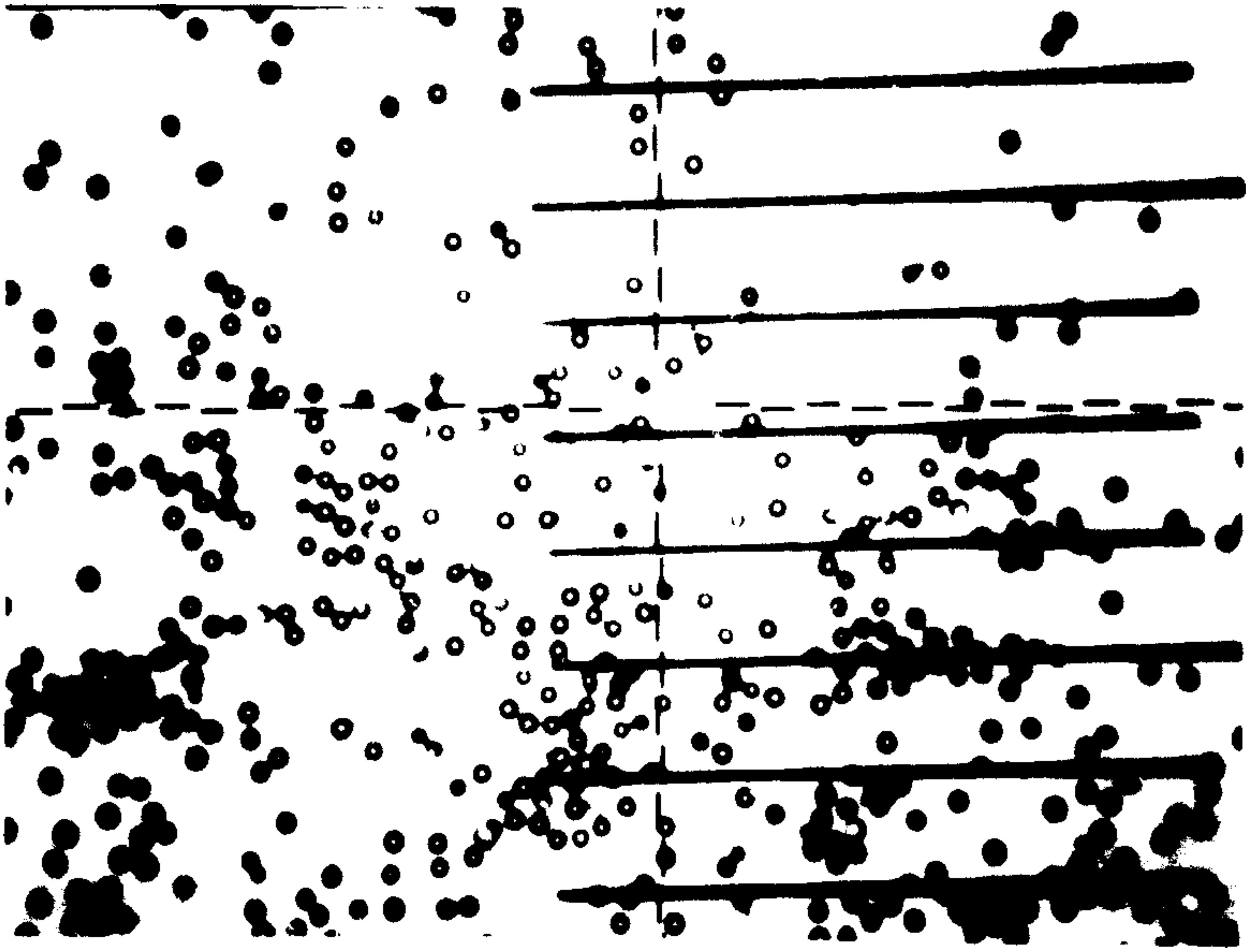

Figure 6.

0.050 mm Glass Particles Magnified 56 Times.

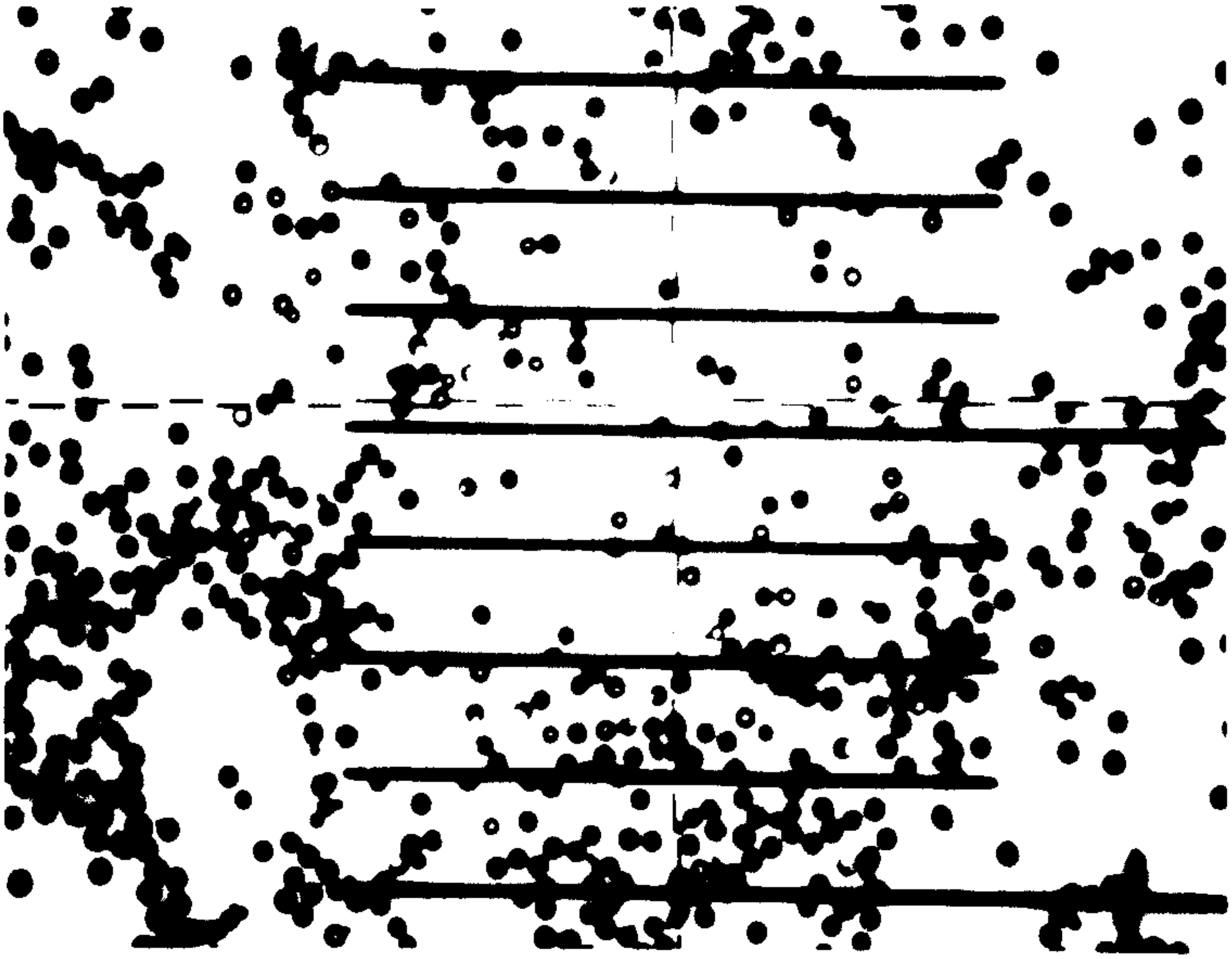

Figure 7.

Nickel Plated 0.050 mm Glass Particles Magnified 56 Times.

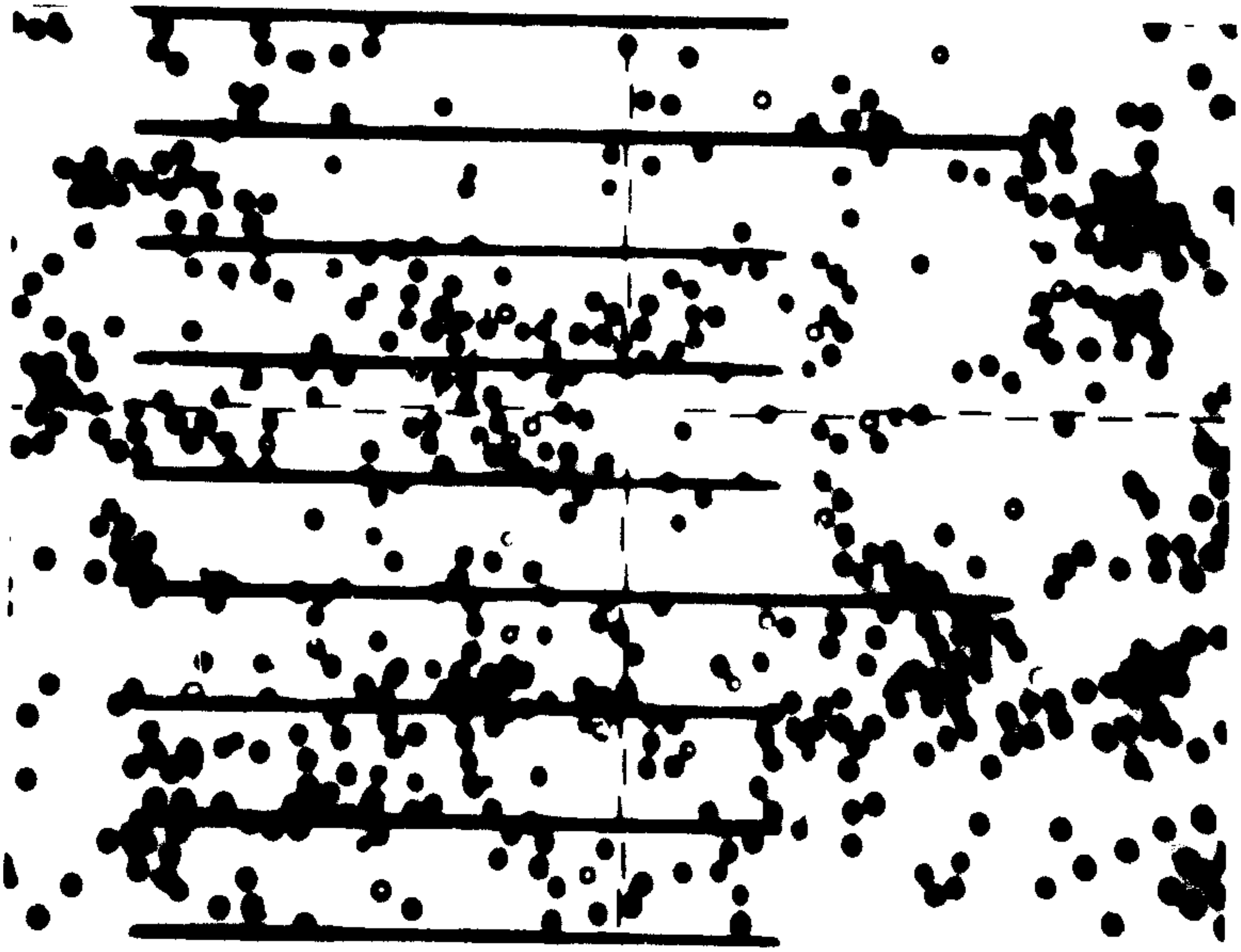

Figure 8.

Nickel Plated 0.050 mm Glass Particles Magnified 56 Times.

A mixture of 0.250 mm to 0.425 mm divinylbenzene-styrene copolymer particles (Fig. 9) was plated. The optimum conditions described for etching, sensitizing, and activating of 1 mm glass particles were also employed in this case. However, treating the polymer surface with concentrated nitric acid prior to conditioning had a significant effect on the nickel nickel coating (Table 2).

Table 2.

Treatment of Divinylbenzene-styrene Copolymer Particles With Nitric Acid

Time (min.)	Concentration (Weight Percent)	Results
0	-	No plating. Testing for 10 hours.
2	70	Onset of plating at 700 sec.
2	35	Onset of plating at 1000 sec.
4	70	Onset of plating at 4500 sec.

The most advantageous treatment consisted of exposing the polymer beads to concentrated nitric acid for 2 minutes (Fig. 10). The resulting deposit was smooth, bright, and evenly distributed on all beads. Longer exposure increased time for the onset of plating due to polymer-solvent interaction and degradation of the polymer surface. Increased exposure also resulted in incomplete plating of all particles (Fig. 11). Tests for adhesion of nickel deposits to polymer surface gave satisfactory results, and no nickel was apparent on the masking tape. Utilizing the optimum conditions for plating of divinylbenzene-styrene copolymer produced bright, even, smooth surfaces on the particles.

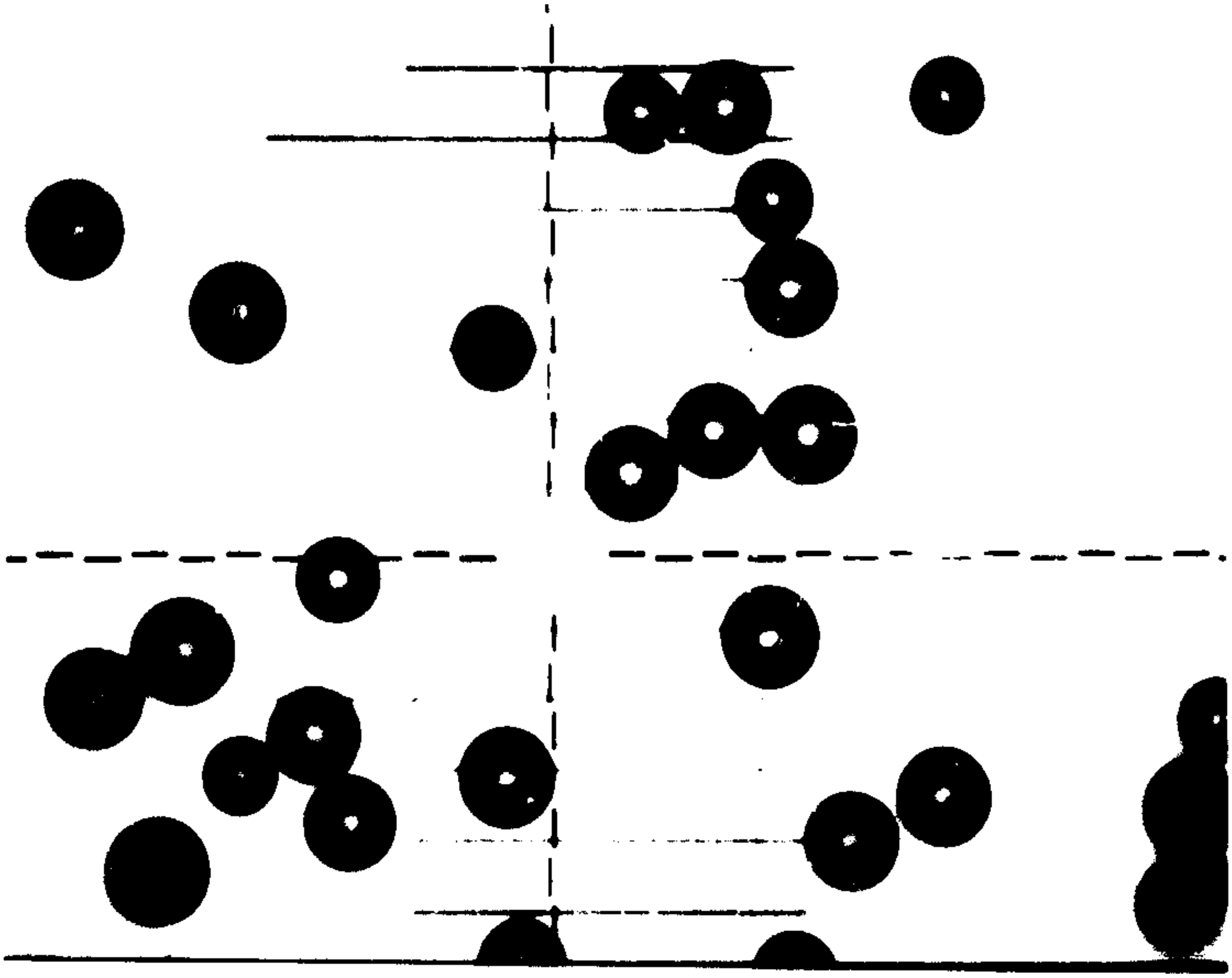

Figure 9.

Divinylbenzene-styrene Copolymer Particles Magnified 32 Times.

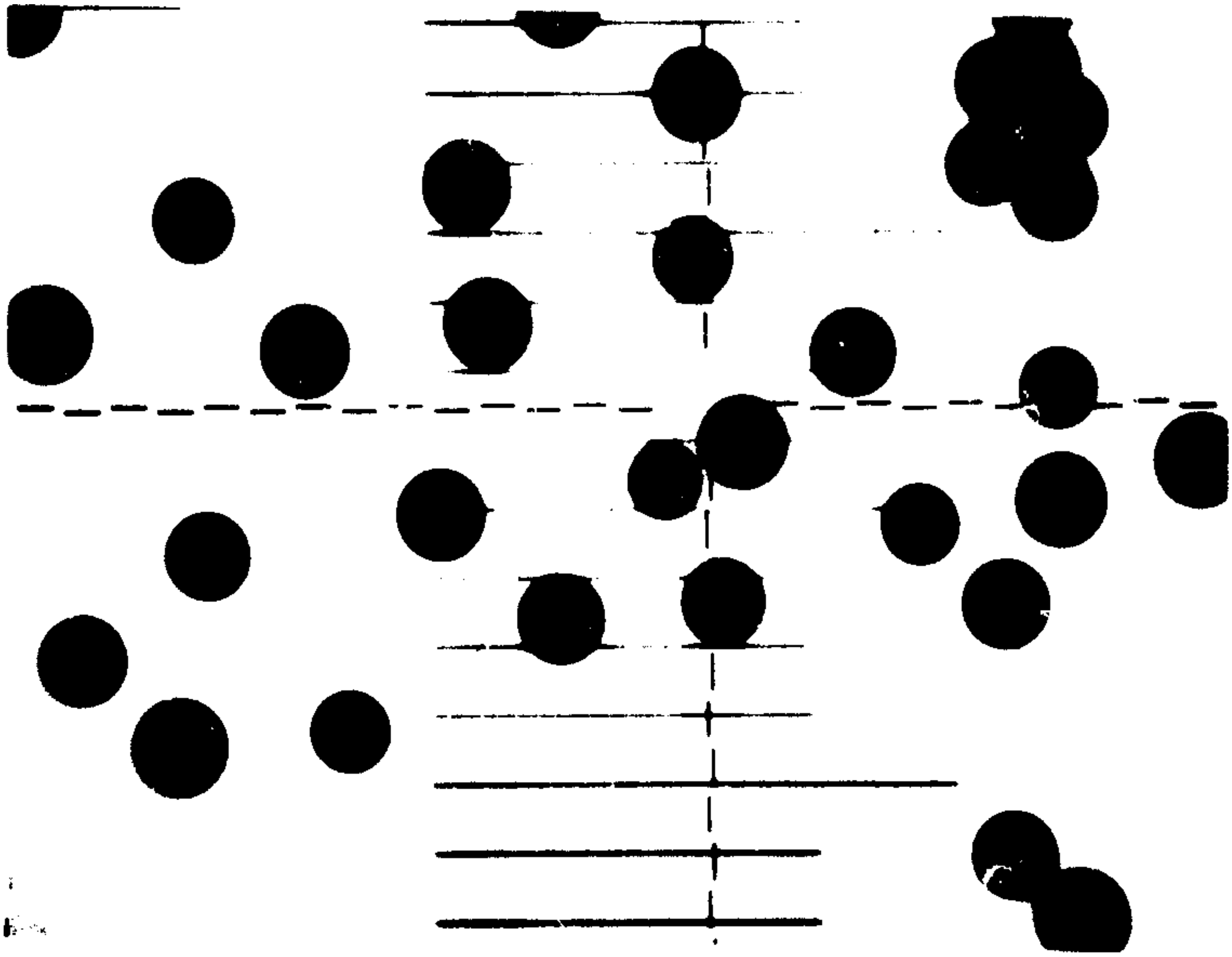

Figure 10.

Plated Divinylbenzene-styrene Copolymer Particles

Treated with Nitric Acid for 2 Minutes. Magnified 32 Times.

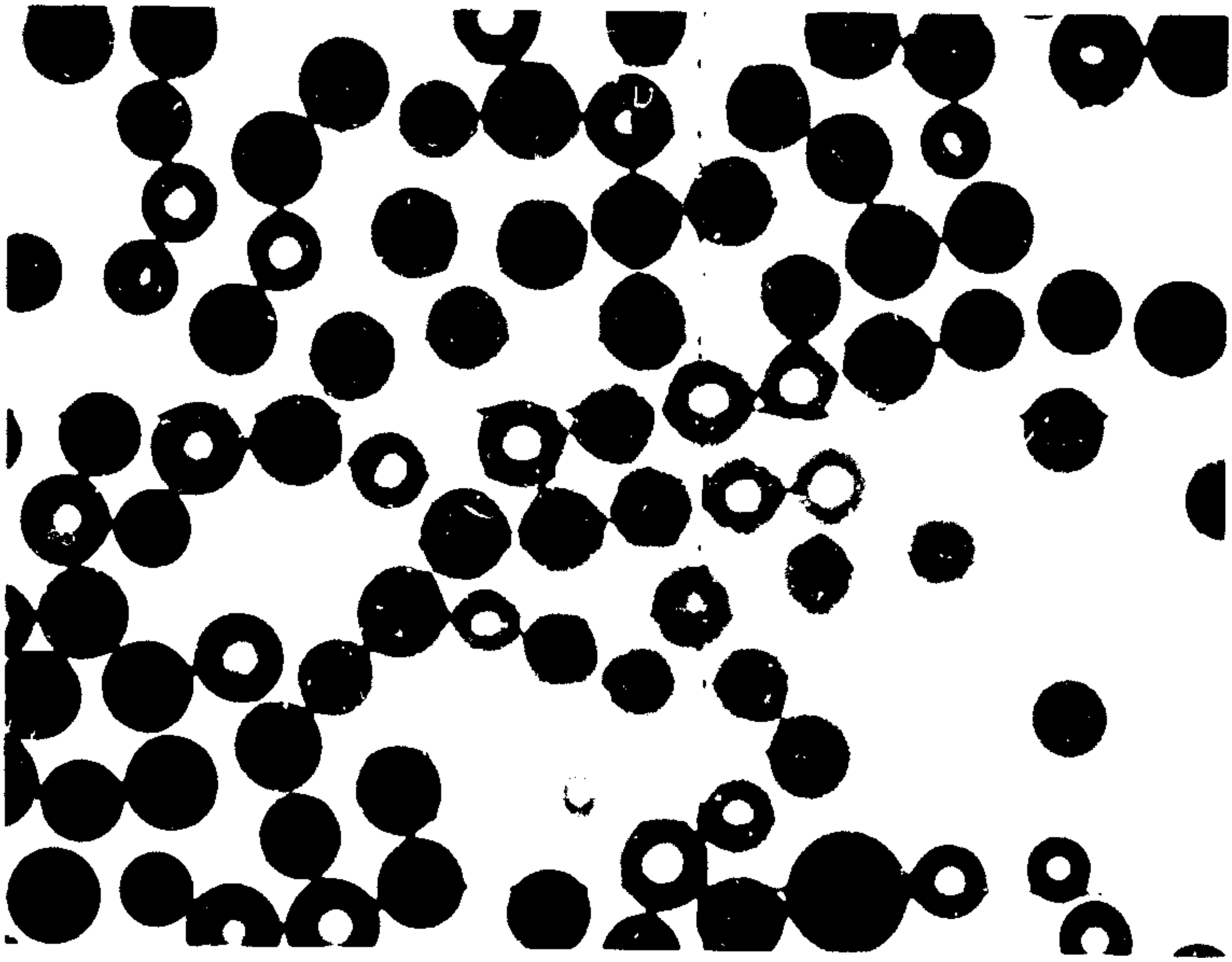

Figure 11.

Plated Divinylbenzene-styrene Copolymer Particles

Treated with Nitric Acid for 4 Minutes. Magnified 32 Times.

CONCLUSIONS AND RECOMMENDATIONS

Electroless nickel plating on glass and divinylbenzene-styrene copolymer surfaces produced satisfactory results when optimum process conditions were used. Coating of 1 mm and 0.100 mm glass particles as well as 0.425 mm to 0.250 mm divinylbenzene-styrene copolymer particles proceeded quite well and created shiny, smooth, even deposits. The electroless nickel plating of 0.050 mm glass particles resulted in good quality deposits; however, the coating was not uniform on all particles. Overall, the electroless nickel plating of particles for use in optical experiments significantly improved the reflection of light from the particles' surfaces without notable increase in the density of the spheres. With slight modifications, the process of electroless nickel plating may be used for coating of particles with diameters smaller than 0.050 mm.

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