IS--5134

**Wet Processing of Palladium for Use in the Tritium Facility
at Westinghouse, Savannah River, SC**

Preparation of Palladium using the Mound Muddy Water Process

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Report IS-5134
Ames, IA 50011
September 30, 1998
Revised, November 10, 1998**

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Introduction

Palladium used at Savannah River for tritium storage is currently obtained from a commercial source. In order to better understand the processes involved in preparing this material, Savannah River is supporting investigations into the chemical reactions used to synthesize this material and into the conditions necessary to produce palladium powder that meets their specifications (Table 1). This better understanding may help to guarantee a continued reliable source for this material in the future. As part of this evaluation, a work-for-others contract between Westinghouse Savannah River Company and the Ames Laboratory Metallurgy & Ceramics Program was initiated. During FY98, the process for producing palladium powder developed in 1986 by Dan Grove of Mound Applied Technologies (USDOE) was studied to understand the processing conditions that lead to changes in morphology in the final product. This report details the results of this study of the Mound Muddy Water process, along with the results of a round-robin analysis of well-characterized palladium samples that was performed by Savannah River and Ames Laboratory.

The Mound Muddy Water process is comprised of three basic wet chemical processes, palladium dissolution, neutralization, and precipitation, with a number of filtration steps to remove unwanted impurity precipitates. In the first step of the Mound process, palladium is dissolved in nitric acid and a trace amount of hydrochloric acid and heated to 100 °C; after the dissolution is complete, the resulting "redwine" solution is filtered to remove undigested material, including platinum and gold. The second step of the Mound process involves neutralization of the redwine with ammonium hydroxide, dilution with water, and addition of

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acetic acid. At higher solution pH (pH 8-9), iron impurities precipitate as iron oxide (hydroxide) and are removed from solution by filtration. In the final step of the Mound process, palladium is precipitated by the addition of a reducing agent, formic acid. It is at this point that the morphology of the palladium product is determined. After precipitation, the resulting solution is filtered to recover the palladium powder, which is subsequently rinsed with water and then dried. The study performed during FY98 examined how the morphology of the palladium product is affected by changes in processing conditions including the rate of addition of formic acid, the initial solution temperature, the initial solution pH, and the palladium concentration. Palladium product samples were analyzed at Ames Laboratory and Savannah River to determine tap density, Microtrac particle size, BET surface area, and palladium nodule size and morphology.

Experimental

The laboratory equipment and components used for palladium dissolution, neutralization, precipitation, and filtration are listed in Appendix 1; a number of photographs of the equipment are also included.

Palladium Dissolution A known mass of palladium (typically approximately 66 grams) is added to a 1 L glass Erlenmeyer flask; concentrated nitric acid (typically 350 mL of 70% HNO₃) and concentrated hydrochloric acid (typically 70 μ L of 37% HCl) are added to the flask, which is covered with a watch glass that is weighted with rubber stoppers. The reaction mixture is stirred and then placed on a hot plate and heated for a minimum of 24 hours; the heating is increased throughout the process, with the solution temperature approximately 70 °C initially and about 100 °C at the end of the dissolution process. Throughout the dissolution, NO_x gas evolves slowly, and is released from the flask. The dissolved palladium redwine solution is cooled to room temperature prior to filtration.

Redwine Filtration The redwine solution is vacuum-filtered using a 2 L filter flask, a filter funnel, and 0.8 μ m pore cellulose nitrate filter paper. Suction is provided by a water aspirator. After transferring the redwine solution to the filter funnel, the 1 L reaction flask is rinsed with deionized water a number of times to ensure complete transfer of the palladium solution. The filter funnel is also rinsed with water after the filtration is complete. The filtrate is subsequently transferred from the filter flask to a 4 L glass Erlenmeyer flask, and the filter flask

is rinsed with water to ensure complete transfer of the solution. At the end of this process, the redwine solution volume is approximately 1 L.

Redwine Neutralization A Teflon-coated magnetic stir bar is placed into the redwine solution in the 4 L glass flask, which is placed into a 40 °C recirculating bath on top of a magnetic stirrer. After allowing the temperature to equilibrate for 10-15 minutes, concentrated ammonium hydroxide (typically 430 mL of 29% NH_4OH) is added to the redwine solution over 10-15 minutes. The NH_4OH is added in approximately 10-mL increments, allowing the reaction mixture to stir between additions. The graduated cylinder(s) used to add the NH_4OH and the sides of the flask are rinsed with water. As the redwine solution is neutralized by NH_4OH , the solution color changes from dark red (in acidic solution), to light red, to orange, to yellow (in neutral to slightly basic solution). The solution pH is checked using pH paper, and NH_4OH is added until the pH is ~8. Acetic acid (typically 4.3 mL of 100% CH_3COOH) is subsequently added to the solution. The graduated cylinder used to add the CH_3COOH and the sides of the flask are rinsed with water. At the end of this process, the resulting “vinegar” solution volume is approximately 2 L. The flask is removed from the recirculator bath and allowed to cool to room temperature, and the solution is allowed to settle for a number of hours prior to filtration.

Vinegar Filtration The vinegar solution is vacuum-filtered using a 2 L filter flask, a filter funnel, and 0.8 μm pore cellulose nitrate filter paper. After transferring the vinegar solution to the filter funnel, the 4 L flask is rinsed with water a number of times to ensure complete transfer of the solution. The filter funnel is also rinsed with water after the filtration is complete. The filtrate is transferred from the filter flask to a 4 L glass beaker, and the filter flask is rinsed with water to ensure complete transfer of the solution. At the end of this process, the vinegar solution volume is approximately 2.5 L. The pH of the solution is adjusted to the desired value by adding HNO_3 and/or NH_4OH to the solution. For palladium processing batches PDHP17-30, pH paper was used to measure the solution pH; for batches PDHP31-43, a pH electrode was used. After the pH is adjusted, water is added to bring the solution volume to the desired value, usually 3 L. For batches PDHP27-30, a 4.5 gallon glass jar was used rather than a 4 L beaker, and the final vinegar solution volume for these batches was 9 L.

Palladium Precipitation The 4 L glass beaker (4.5 gallon jar) containing the vinegar solution is placed into a temperature-controlled recirculating bath. The solution is stirred using a

laboratory mixer with a fixed, dual-blade polypropylene paddle (approximately 1.5" wide by 0.75" tall), mounted in an off-center mixing configuration, at a speed of 1250 rpm. After the solution has reached the desired temperature, formic acid is added to the solution to precipitate the palladium. Formic acid is added at the surface of the solution using a tubing pump and tygon pump tubing, at the desired addition rate and length of time required to add the desired volume of formic acid (typically 70 mL). A small amount of water (~50 mL) is usually added, to rinse the tygon pump tubing. As formic acid is added, the solution changes color from yellow to black, usually before the formic acid addition is complete. After the formic acid addition is complete, the solution bubbles, as reaction gases (carbon dioxide and ammonia) evolve from solution. The solution temperature increases during the precipitation reaction, increasing approximately 5 to 10 °C, depending on the reaction conditions used. The solution pH decreases to a value of pH ~2-3 after the formic acid is added. However, as the reaction proceeds, the pH increases, reaching a value of pH ~8 at the end of the precipitation reaction for most of the processing batches. The precipitation reaction is usually complete within 10 minutes after the start of formic acid addition. The solution is stirred throughout the precipitation reaction and for a period of approximately 20 minutes after the reaction is complete (a total of 30 minutes mixing time). The mixer is then turned off. The beaker (or glass jar) is removed from the recirculator bath, and the palladium precipitate solution is allowed to cool to room temperature.

Palladium Filtration, Drying, and Sieving The palladium precipitate solution is vacuum-filtered using a 2 L filter flask, a filter funnel, and 0.8 µm pore cellulose nitrate filter paper. The solution is initially decanted (and filtered) from the palladium precipitate. The precipitate remaining in the beaker is rinsed four or five times with approximately 250-mL aliquots of water, decanting the water from the palladium after each rinsing. The palladium precipitate is subsequently transferred from the beaker to the filter funnel, using water to "rinse" the palladium into the filter funnel. After the water is removed, the palladium is transferred from the filter funnel to a 6" watch glass using a spatula, and the watch glass is placed into a 110 °C drying oven. (A small amount of palladium, typically 1-2 grams, coats the polypropylene mixer paddle; this palladium is removed from the paddle using a spatula and is usually added to the rest of the palladium precipitate, for drying.) The palladium is dried for a minimum of 24 hours. After drying, the watch glass and palladium are placed into a dessicator and allowed to cool to

room temperature. The palladium is weighed after it has cooled to room temperature. The dried palladium is manually sieved, using a 100-mesh nylon sieve, lid, and receiving tray: palladium is transferred from the watch glass to a 2-ounce glass bottle, using a spatula; the bottle is shaken to break up any large chunks or clumps of palladium; the palladium is transferred from the 2-ounce glass bottle to the sieve, and manually shaken. A quantity of approximately 10 grams can be sieved at a time, with the small sieve used. The sieved fraction is transferred from the receiving tray to a 4-ounce glass bottle, and the mass of the sieved fraction is determined at the end of the sieving process.

Palladium Powder Analysis Palladium powder samples were characterized to determine the tap density, particle size, surface area, and palladium nodule size and morphology. Tap density and some Microtrac particle size analyses were performed at the Ames Laboratory Materials Preparation Center (MPC). The tap density analysis was performed using approximately 20 grams of palladium and a JEL Stampfvolumeter model STAV2003, performing 5000 taps to determine the tap density. The Microtrac particle size analysis was performed by mixing approximately 0.1 grams of palladium with about 10 mL of an aqueous solution containing 4% (by weight) sodium polyphosphate in a glass vial, sonicating the mixture for 3 minutes using a Branson model 1510 ultrasonic bath, and measuring the particle size distribution using a Microtrac II Particle Size Analyzer. Some BET surface area measurements were performed by the Iowa State University (ISU) Materials Science & Engineering department. The surface area analysis was performed by placing approximately 5 grams of palladium into a sample cell, degassing the sample, and determining the BET surface area using a Quantachrome Corporation model Autosorb-1. For palladium processing batches PDHP17-43, a portion of the palladium was sent to Savannah River for Microtrac particle size, BET surface area, and SEM characterization of palladium nodule size and morphology.

Results & Discussion

Palladium Round-Robin Sample Analyses Three palladium powder samples that had been characterized at Savannah River were analyzed at Ames Laboratory, to determine if the methods and instrumentation used for tap density, Microtrac particle size, and BET surface area analyses performed at the Ames Laboratory MPC and the ISU Materials Science & Engineering

department yielded accurate values. These samples were palladium standard samples, received from Savannah River. The tap density, particle size, and surface area values determined for these three samples are listed in Table 2, along with the analytical results obtained at Savannah River for the samples. A comparison of the results indicates that the agreement between the values obtained at Ames Laboratory and those at Savannah River is reasonably good. The tap density values differ by approximately +/- 4%, relative, and the BET surface area values differ by +/- 5-8%. The Microtrac particle size results for sample 44148 are the same, within about 1 μm , and those for sample 44174 are the same, within 2 μm ; the values for sample 3904-1 differ by about 2-5 μm . Thus, the methods and instrumentation used for tap density, Microtrac particle size, and BET surface area analyses at Ames Laboratory and Savannah River yield results that are comparable, for the palladium powder samples analyzed.

Palladium Processing Batches PDHP17-43 Twenty-seven palladium batches were made at Ames Laboratory using the Mound process, as described above. The results for these batches and a description of the processing conditions used to produce these batches are given in Table 3 and Appendix 2, respectively. The tap density results in Table 3 were determined at Ames Laboratory; the Microtrac particle size and BET surface area values were determined at Savannah River. A number of processing batches, PDHP1-16, were made at the beginning of this study, but the results are not included here. The processing conditions for these initial batches differed from the experimental conditions used for batches PDHP17-43 in a number of ways: a variety of containers, glass flasks and beakers and polyethylene beakers, were used as reaction vessels for the palladium precipitation step; a magnetic stirrer rather than a laboratory mixer was used during the precipitation reaction; and the formic acid addition rate (<5 mL/min) was much lower than the rates used for batches PDHP17-43. The palladium sponge starting material used for these initial batches consisted of fines as well as larger particles of palladium (~1 mm diameter) that was much more difficult to dissolve than the palladium sponge used for batches PDHP17-43, which consisted only of fine particles. (For batches PDHP26 and 30-43, palladium precipitate produced in previous batches was redissolved; this palladium is referred to as "reprocess" palladium in Appendix 2, and dissolved very easily.) For many of the initial batches (PDHP1-16), hydrogen peroxide was added to the nitric acid and hydrochloric acid mixture to improve the palladium dissolution. A microwave digestion system (CEM model

MDS-2100) was used for palladium dissolution for two initial processing batches; the digestion vessels for this system are designed for dissolving a few grams of material, not the ~66 grams of palladium used for most of the PDHP17-43 batches, so only two microwave digestion batches were done.

Processing batches PDHP17-43 were made in a more systematic manner than the initial batches. A single variable in the reaction conditions was changed, with the remainder of the conditions more consistent from batch-to-batch, although there were some differences in the individual batches. For batches PDHP17-25 and 31-43, the palladium concentration was approximately 22 g/L (65-67 grams of palladium dissolved in a 3 L volume of vinegar solution); the formic acid addition rate, initial solution temperature, and initial solution pH were varied in order to study the effect of changes in these reaction conditions. For batches PDHP25-30, the palladium concentration was varied, ranging from 5 to 22 g/L.

For a number of processing batches, the mixer was turned off momentarily during the precipitation reaction to minimize the amount of palladium and solution lost from the beaker, as a result of excessive bubbling in solution (see Table 3). For batches PDHP24, 25, 31, and 32, a larger volume of formic acid was added, and it is believed that the larger amount of formic acid resulted in excessive bubbling in solution during the precipitation reaction. Batches PDHP21, 22, and 23, which were also made using a larger volume of formic acid, did not bubble excessively. However, these batches were made at lower temperatures or higher initial solution pH, which is believed to have had the effect of minimizing the reactivity and bubbling in solution. No systematic study of the effect of mixing speed or interruptions in mixing was done, so the effect of turning off the mixer momentarily during the precipitation reaction for these batches is unknown. Batches PDHP37, 39, 41, and 42 were made using identical reaction conditions. However, for PDHP39 and 41, the mixer was turned off momentarily (~5-10 seconds for PDHP39 and ~30 seconds for PDHP41) during the precipitation reaction to minimize the amount of palladium and solution that was lost from the beaker as a result of excessive bubbling in solution. The reason for this difference in reactivity for these two batches is not clear. The fact that excessive bubbling in solution occurred indicates a difference in the processing conditions for these two batches (from some unknown source), and this unknown difference as well as the interruption in mixing are assumed to have had some effect (of unknown

extent) on the resulting tap density, particle size, and surface area of the palladium precipitate that formed.

A variable amount of a form of palladium termed “bright” palladium formed during the precipitation reaction for batches PDHP17-43. This palladium, which consists of shiny, silver-colored specks and/or flakes rather than the desired black-colored palladium powder, comprised less than 1% to approximately 5% of the mass of the palladium precipitate formed in batches PDHP17-43. The bright palladium formed primarily on the walls of the glass beaker. Usually this palladium was removed from the walls during the precipitation reaction by the mixing in solution, but occasionally the beaker remained coated with a layer of bright palladium after the precipitation reaction was complete. The amount of bright palladium that formed was generally larger for those batches that were made at low temperature and slow formic acid addition rates. However, the quality and cleanliness of the glass beaker walls also seemed to have some effect on the amount of bright palladium that formed, even at high temperatures and fast addition rates. For instance for batches PDHP31, 33, and 36 that were made using the same 4 L glass beaker, a relatively large amount of bright palladium formed, coating the walls of the beaker after the precipitation reaction was complete (see Appendix 2). Although the beaker was acid-cleaned using a mixture of nitric and hydrochloric acids between processing batches, a relatively large amount of bright palladium formed using this beaker. Subsequent batches were precipitated using a different beaker, with better results.

Formic Acid Addition Rate The formic acid addition rate used for the palladium precipitation step was varied for processing batches PDHP17, 18, 19, and 20, using addition rates of 20, 40, 60, and 77 mL/min, respectively. The initial solution pH for these four batches was approximately 6 (measured using pH paper), and the initial solution temperature was 58-59 °C. Analysis of the results for the palladium powder samples produced indicates that the tap density decreases (1.696, 1.611, 1.491, and 0.975 g/cc) and the surface area increases (0.633, 0.767, 0.755, and 1.222 m²/g) as the formic acid addition rate increases. The particle size decreases as the formic acid addition rate increases, with d₅₀ values of 35.37, 26.88, 25.82, and 23.63 μm for batches PDHP17, 18, 19, and 20. However, the effect is not as pronounced as the variation in the tap density and surface area values, particularly for addition rates between 40 and 77 mL/min, where the particle sizes differ by only about 10-20%.

Initial Solution Temperature The initial solution temperature at which the palladium precipitation reaction was performed was varied for processing batches PDHP21, 22, and 19, using values of 40, 50, and 58 °C, respectively. The initial solution pH for these three batches was approximately 6 (measured using pH paper), and the formic acid addition rate was 60 mL/min. At low temperature, the incubation time increases and the precipitation reaction rate decreases; a very long incubation time, 8 minutes between the start of formic acid addition and the start of bubbling in solution, was observed for the 40 °C temperature processing batch PDHP21 (see Appendix 2). The particle size decreases with increasing temperature, with d_{50} values of 60.70, 34.57, and 25.82 μm , respectively, for batches PDHP21, 22, and 19. The tap density values increase with increasing temperature, with values of 0.794, 1.062, and 1.491 g/cc. The surface area values for these three batches are 1.852, 0.785, and 0.755 m^2/g .

Initial Solution pH The initial solution pH at which the palladium precipitation reaction was performed was varied for processing batches PDHP23, 19, and 24, using values of pH 9, 6, and 3, respectively (measured using pH paper). The initial solution temperature for these three batches was approximately 60 °C, and the formic acid addition rate was 60 mL/min. For batch PDHP23, made at high initial solution pH, the palladium particle size is larger than that for batches PDHP19 and 24. The d_{50} and d_{75} values for PDHP23 are 40.06 and 68.89 μm ; the corresponding values for batches 19 and 24 are 25.82 and 54.12 μm and 33.58 and 55.35 μm . The tap density values for batches PDHP23, 19, and 24 are 1.142, 1.491, and 0.65 g/cc, respectively, and the surface area values are 0.697, 0.755, and 2.692 m^2/g . Thus it appears that at low initial solution pH (pH 3 for batch PDHP24), palladium powder having low tap density and high surface area is produced. However, it should be noted that batch PDHP24 is one of the batches for which the mixer was turned off momentarily during the precipitation reaction, due to excessive bubbling in solution, so trends based on the tap density and surface area (and particle size) values for PDHP24 may be somewhat suspect.

Batches PDHP34, 37, and 36 form a set for which the palladium precipitation was performed using essentially identical reaction conditions (~70 mL/min formic acid addition rate, 60 °C solution temperature, 22 g/L palladium, and nearly constant palladium-to-formic acid concentration ratio), except for the initial solution pH, which was 9, 8, and 7, respectively. For batches PDHP34, 37, and 36, the surface area increases with decreasing pH (0.83, 1.19, and 1.90

m²/g), and the tap density values are 0.885, 1.148, and 0.753 g/cc. For batch PDHP34, made at high initial solution pH 9, the particle size is larger than that for batches 37 (pH 8) and 36 (pH 7). The d₅₀ and d₇₅ values for PDHP34 are 78.0 and 119.1 μm; the corresponding values for batches 37 and 36 are 35.7 and 65.2 μm and 28.3 and 58.1 μm. The particle size for PDHP34 is higher than the specification for particle size and significantly larger than that for batch PDHP23, which was also made at initial pH 9 (see preceding paragraph). However, the formic acid addition rate and the palladium-to-formic acid concentration ratio for batches PDHP34 and 23 were not the same, so differences in tap density, particle size, and surface area values for these two batches are not unexpected.

Palladium Concentration The palladium concentration was varied for processing batches PDHP25-30. For batches PDHP27-30, which were made using initial solution temperature 50 °C, pH 6, and a 60 mL/min formic acid addition rate, the palladium concentration varies from 5 to 15 g/L (in a 9 L volume of solution). The tap density values for these four batches are all low (0.825, 0.616, 0.809, and 0.84 g/cc for batches PDHP28, 29, 27, and 30, respectively) compared to the 0.9-1.2 g/cc specification, and the surface area values are all high (1.74, 3.37, 2.27, and 1.93 m²/g) compared to the 0.9-1.2 m²/g specification. The particle sizes for these batches are within specifications, except for batch PDHP29, which has a very small particle size (d₂₅ = 5.4, d₅₀ = 11.4, and d₇₅ = 20.0 μm). This batch has the lowest palladium-to-formic acid concentration ratio (46.5 g Pd / 180 mL formic acid), and has the smallest particle size, lowest tap density, and highest surface area for these four batches. The palladium-to-formic acid concentration ratio clearly affects the characteristics of the palladium precipitate formed and is an important parameter in the processing conditions. Batches PDHP28 and 30, which have a factor of 3 difference in palladium concentration but a constant palladium-to-formic acid concentration ratio, have tap density (0.825 and 0.84 g/cc), particle size (d₅₀ = 37.9 and 31.5 μm), and surface area (1.74 and 1.93 m²/g) values that are quite similar. Thus, it appears that maintaining a constant palladium-to-formic acid concentration ratio is important for obtaining palladium powders having consistent tap density, particle size, and surface area characteristics. Since this concentration ratio is not constant for all of the processing batches PDHP17-43, the variability in the palladium-to-formic acid concentration ratio may account for some variability in the experimental results.

For PDHP25 and 26, the palladium concentration differs by a factor of 2 (22 and 11 g/L, respectively, in a 3 L volume). However, no definitive conclusions regarding the effect of the variation in palladium concentration can be made for these batches: the nitric acid, hydrochloric acid, ammonium hydroxide, and acetic acid reagent volumes also differ by a factor of approximately 2 for these batches (see Appendix 2); the palladium-to-formic acid concentration ratio is not constant; and PDHP25 is one of the batches for which the mixer was turned off momentarily during the precipitation reaction, due to excessive bubbling in solution.

Reproducibility A number of batches, PDHP37, 39, 41, and 42, were prepared using identical reaction conditions - 70 mL/min formic acid addition rate, initial solution temperature 60 °C and pH 8, and a constant palladium-to-formic acid concentration ratio. As indicated in Table 3, for two of these batches, PDHP39 and 41, the mixer was turned off momentarily (~5-10 seconds for PDHP39 and ~30 seconds for PDHP41) during the precipitation reaction to minimize the amount of palladium and solution that was lost from the beaker, as a result of excessive bubbling in solution. It should be noted that the procedure used for formic acid addition for these four batches differed slightly. For PDHP37 and 39, the tygon pump tubing used to add formic acid was empty initially, and the pump was turned on for 1 minute to deliver formic acid. After 1 minute, the tubing was removed from the formic acid reagent bottle and placed into a beaker containing ~50 mL of water, which was pumped through the tubing to rinse the formic acid remaining in the tubing into the palladium solution. For PDHP41 and 42, the tygon pump tubing was completely filled with formic acid initially, and the pump was turned on for 1 minute to deliver formic acid and then turned off. After the precipitation reaction was complete, the formic acid remaining in the tubing was pumped into a small waste container. The tap densities for these four samples are 1.148, 1.016, 0.784, and 1.049 g/cc, respectively. The tap densities for PDHP37, 39, and 42 differ by approximately 10%, relative; however, the value for PDHP41 is significantly lower. The momentary stop in mixing during the precipitation reaction, particularly for batch PDHP41, may have contributed to the differences in tap density observed. However, the (unknown) source of the apparent difference in reactivity that caused the solution to bubble excessively may itself be a contributing factor in the differences in tap density observed. The Microtrac particle sizes for these four batches differ by a significant amount. The particle size for batch PDHP42 is large, with d_{25} , d_{50} , and d_{75} values of 25.2, 55.3, and 87.8 μm , respectively.

The d_{50} and d_{75} values for this batch are higher than the specifications for particle size. The values for the other three batches are all within the particle size specifications. However, batch PDHP39 has a relatively small particle size, with d_{25} , d_{50} , and d_{75} values of 13.3, 28.6, and 44.8 μm . Batches PDHP37 and 41 have fairly similar d_{25} (15.8 and 17.3 μm), d_{50} (35.7 and 39.5 μm), and d_{75} (65.2 and 61.8 μm) particle size values. The BET surface area values for batches PDHP37, 39, 41, and 42 are also significantly different, with values of 1.19, 1.40, 1.91, and 1.23 m^2/g , respectively. The increase in surface area for batches PDHP39 and 41 was expected, based on the general trends observed for other batches (PDHP24, 25, 31, and 32) that had excessive bubbling in solution during the precipitation reaction. For batch PDHP39, the mixer was turned off momentarily (~ 5 -10 seconds) during the precipitation reaction due to excessive bubbling in solution, and the surface area is slightly larger (1.40 m^2/g) than the values for PDHP37 and 42. For batch PDHP41, the bubbling in solution during the precipitation reaction was more excessive, and the mixer was turned off for approximately 30 seconds. The surface area for PDHP41 is significantly larger (1.91 m^2/g).

Batch PDHP43 was also made using the same reaction conditions as those for batches PDHP37, 39, 41, and 42. However, the mixer speed was less than 1250 rpm initially (presumably about 500 rpm) during the precipitation reaction; at some point after formic acid addition began, the mixer speed was set to 1250 rpm. The lower initial mixing speed resulted in a slightly higher tap density for batch PDHP43 (1.231 g/cc) than the values obtained for the other four batches, and a slightly lower surface area (1.02 m^2/g). The particle size for PDHP43 was larger than that for the other four batches, with d_{25} , d_{50} , and d_{75} values of 26.2, 56.9, and 93.9 μm . However, since only about half of the palladium precipitate passed through the 100 mesh, 150 μm , sieve (see Appendix 2), the d_{25} , d_{50} , and d_{75} values underestimate the actual particle size for batch PDHP43. The mixing speed and effectiveness clearly affects the characteristics of the palladium precipitate formed, but no systematic study of this effect was performed in this work.

SEM Characterization of Palladium Powders The nodule size and morphology of the palladium powders was characterized by scanning electron microscopy (SEM) performed at Savannah River. SEM photomicrographs for all 27 batches, PDHP17-43, were acquired, but only three examples are included in this report. The palladium powder should consist of clusters of uniform, smooth, spherical particles. For some of the batches, some variation in the size of

the nodules was observed, as shown in the SEM photomicrographs in Figure 1 for batch PDHP18. The photomicrographs in Figure 2 for PDHP24 include some lower magnification data, showing what appears to be a “bright” palladium speck in the center of the upper right photograph. The palladium morphology for PDHP37, a batch that met all the tap density, Microtrac particle size, and BET surface area specifications, is shown in Figure 3.

Trends in Processing Conditions and Palladium Powder Characteristics The only fairly consistent trend observed in this study is the inverse relationship of tap density and BET surface area. Even this trend has an exception. The variation of the tap density with changing pH is not monotonic (i.e. the tap density is low at both high and low pH, but high at intermediate pH), whereas the surface area is high at low pH and decreases with increasing pH. The surface area also exhibits some unusual behavior where, for instance, the surface area drops as the reaction temperature rises from 40 to 50 °C but is roughly the same at 50 and 60 °C. There is also no definite correlation between variations in the tap density and in the Microtrac particle sizes. These parameters are inversely related as temperature is varied but correlated as the palladium-to-formic acid concentration ratio is varied. As a result of the complex nature of this precipitation reaction, simple linear trends and observations are not obvious from this data. Therefore, multiple linear regression fits of the varied parameters and analytical measurements were performed in order to predict processing conditions that would result in palladium powder meeting specifications.

Modeling of Reaction Conditions The tap density, particle size, and surface area values determined for processing batches PDHP17-24 were used to generate a model of formic acid addition rate, initial solution temperature, and initial solution pH that was designed to yield a set of “optimized” processing conditions that would enable palladium powder samples to be produced that met the tap density, particle size (d_{50}), and surface area specifications. This model was generated by performing a multiple linear regression fit of addition rate, temperature, and pH, including linear and quadratic terms in each plus a constant term. A number of batches, PDHP33-38, were prepared using this model to predict the formic acid addition rate, initial solution temperature, and initial solution pH processing conditions to use for these batches. .

Batch PDHP33 was prepared using a formic acid addition rate of 63 mL/min, initial solution temperature 60 °C, and initial solution pH 6. The tap density (1.048 g/cc) is within

specification, as are the d_{25} and d_{50} particle size values (19.5 and 41.3 μm). The surface area (1.36 m^2/g) and the d_{75} particle size (70.2 μm) values for PDHP33 are slightly higher than the specifications. Batch PDHP34 was prepared using a formic acid addition rate of 71 mL/min, initial solution temperature 60 $^{\circ}\text{C}$, and initial solution pH 9. The tap density (0.885 g/cc) and surface area (0.83 m^2/g) values are slightly lower than the specifications. The particle size for PDHP34, however, is significantly higher than the specifications (d_{25} , d_{50} , and d_{75} values of 40.1, 78.0, and 119.1 μm). PDHP35 was prepared at 60 mL/min, 55 $^{\circ}\text{C}$, and pH 5.5. The tap density (0.908 g/cc) and particle size (d_{50} = 42.6 μm) values are within specifications, but the surface area (1.68 m^2/g) is too high. Batch PDHP36, prepared at 70 mL/min, 60 $^{\circ}\text{C}$, and pH 7, has a low tap density (0.753 g/cc) and a high surface area (1.90 m^2/g), but the particle size is within specifications. Batch PDHP37, prepared at 70 mL/min, 60 $^{\circ}\text{C}$, and pH 8, has tap density (1.148 g/cc), particle size (d_{50} = 35.7 μm), and surface area (1.19 m^2/g) values that are all within the specifications. PDHP38 was prepared using a 50 mL/min formic acid addition rate, 55 $^{\circ}\text{C}$ initial temperature, and initial solution pH 5. The tap density (1.114 g/cc) is within specification. However, the particle size (d_{50} = 49.7 μm) and surface area (1.23 m^2/g) values for this batch are slightly higher than the specifications. The observed weaknesses of this model may be attributed to the relatively small set of modeled data (8 batches) and the neglect of the effects of variations in the palladium-to-formic acid concentration ratio. Despite these limitations, the predicted conditions yielded palladium powder samples that met specifications in one or more areas for processing conditions that varied considerably in formic acid addition rate (50-71 mL/min), initial solution temperature (55-60 $^{\circ}\text{C}$), and initial solution pH (pH 5-9).

A more extensive modeling of reaction conditions and palladium powder characteristics was performed using the tap density, particle size, and surface area results for batches PDHP17-38. This model was generated by performing a multiple linear regression fit of formic acid addition rate, initial solution temperature, initial solution pH, and palladium-to-formic acid concentration ratio, including linear and quadratic terms for each variable plus a constant term. Some of these terms were eliminated based on iterative tests of the significance of these terms to the overall quality of the fit. A separate fit of the addition rate, temperature, pH, and palladium-to-formic acid ratio variables was performed for each of the three modeled palladium parameters: tap density, d_{50} particle size, and surface area. For tap density, the best fit was

obtained using linear terms in addition rate, temperature, and pH, plus quadratic terms for pH and palladium-to-formic acid ratio. For particle size, the best fit was obtained using linear terms in temperature and palladium-to-formic acid ratio, and linear and quadratic terms in pH. The best fit of the surface area was obtained using linear terms in addition rate, temperature, pH, and palladium-to-formic acid ratio, with a quadratic term in temperature. A plot of the modeled reaction conditions required to produce palladium having a tap density of 1.0 g/cc for a fixed palladium-to-formic acid ratio (0.943 g Pd / mL formic acid) is shown in Figure 4. The plot shows a surface of temperature, addition rate, and pH values that, based on the model, should yield palladium having tap density 1.0 g/cc. A plot of the modeled temperature and pH reaction conditions, and the resulting d_{50} particle sizes for a fixed palladium-to-formic acid concentration ratio (0.943 g Pd / mL formic acid) is shown in Figure 5. For particle size, no significant dependence on the formic acid addition rate was observed in the fit, so no addition rate dependence is plotted in Figure 5. A plot of the modeled reaction conditions required to produce palladium having a surface area of 1.0 m²/g for a fixed palladium-to-formic acid ratio (0.943 g Pd / mL formic acid) is shown in Figure 6, indicating the combination of addition rate, temperature, and pH conditions required to produce 1.0 m²/g surface area palladium.

Concluding Remarks

This work details the results of our investigation of the Mound Muddy Water process for the production of palladium powder. The investigation included an examination of the parameters affecting the morphology of the product, including the initial pH and temperature of the “vinegar” solution, the addition rate of formic acid to the vinegar solution, and the ratio of formic acid to palladium in the reaction vessel. These parameters all had a significant effect on the relevant specifications for this material including tap density, surface area, and particle size distribution. The range of controllable factors allows one to select a range of conditions that satisfy these specifications. Our statistical fit of these experiments provides a means for predicting the product characteristics for a given set of experimental conditions. There appear to be other significant factors not examined in this work, including the mixing rate of the reaction solution. We attempted to hold this factor constant during these experiments, but there were occasional instances of a short time period of low or no mixing, and these cases appear to have

led to significant variations in the product. Another improvement in the uniformity of the results may be achieved by adding the formic acid into the reaction vessel nearer the mixer or at multiple locations within the vessel, rather than at the surface. However, utilizing only the factors investigated here, it should be possible to produce palladium that meets specifications with reasonable reproducibility.

Acknowledgments

Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University, under contract number W-7405-Eng-82. The authors wish to thank Mr. Robert Terpstra of the Ames Laboratory MPC for performing tap density and Microtrac particle size analyses on the palladium powder samples and Dr. Mufit Akinc and Mr. Kurt Ulmer of the ISU Materials Science & Engineering department for performing BET surface area analyses.

Table 1. Palladium Powder Specifications

	Specifications	
Tap density	0.9 - 1.2	g/cc
BET surface area	0.9 - 1.2	m ² /g
Nodule size	0.3 - 0.8	μm
Microtrac particle size		
25%<	10-26	μm
50%<	21-47	μm
75%<	30-67	μm
Chemical impurities		
C	<100	wppm
S	<5	wppm
N	<200	wppm
O	<1200	wppm
Cl	<150	wppm
B, Si, P, Br	<50 total	wppm
Na, K	<100 total	wppm
Fe, Cr, Ni, Mo	<60 total	wppm
Pt, Rh, Ru, Os, Ir, Au, Ag	<1500 total	wppm
As, Cd, Sn, Sb, Pb, Bi, Hg, Tl, Zn, Cu	<50 each, <100 total	wppm
All other elements-GDMS		wppm
All other elements - ICPMS	<10 each, <100 total	wppm

Table 2. Characterization of Palladium Round-Robin Samples

		Palladium Sample	
	3904-1	44148	44174
Tap density (g/cc)	1.131 (1.18)	1.194 (1.15)	1.194 (1.2)
Microtrac particle size			
d ₂₅ (μm)	14.31 (12.5)	22.32 (22.3)	19.3 (17.7)
d ₅₀ (μm)	26.65 (23.1)	36.05 (36.6)	32.47 (30.8)
d ₇₅ (μm)	42.91 (38.2)	52.03 (53.2)	47.90 (46.1)
BET surface area (m ² /g)	1.094 (1.15)	1.037 (0.96)	1.057 (1.0)

The values in parentheses are the analysis results obtained at Savannah River.

Table 3. Experimental Conditions and Analysis Results for Palladium Processing Batches PDHP17-43

Batch	Formic Acid addition rate (mL/min) / volume (mL)	Initial / Final Temperature (°C) *	Initial / Final Solution pH **	Volume (L)	Palladium Conc. (g/L)	Tap Density (g/cc)	Microtrac Particle Size d ₂₅ / d ₅₀ / d ₇₅ (µm)	BET Surface Area (m ² /g)
PDHP17	20 / 67	59 / 64	6 / 8	3	22.5	1.696	17.14 / 35.37 / 70.19	0.633
PDHP18	40 / 67	59 / 64	6 / 8	3	21.6	1.611	11.30 / 26.88 / 55.01	0.767
PDHP19	60 / 70	58 / 64	6 / 8	3	22.0	1.491	12.27 / 25.82 / 54.12	0.7553
PDHP20	77 / 77	59 / 65	6 / 8	3	22.4	0.975	12.27 / 23.63 / 44.54	1.2216
PDHP21	60 / 80	40 / 49	6 / 8	3	22.4	0.794	36.85 / 60.70 / 86.73	1.8520
PDHP22	60 / 80	50 / 56	6 / 8	3	22.4	1.062	20.19 / 34.57 / 53.43	0.7852
PDHP23	60 / 80	60 / 65	9 / 8	3	22.1	1.142	21.57 / 40.06 / 68.89	0.6972
PDHP24†	60 / 85	60 / 65	3 / 7	3	22.1	0.65	14.60 / 33.58 / 55.35	2.6915
PDHP25†	75 / 81	60 / 66	6 / 7.5	3	21.6	1.076	14.8 / 34.8 / 61.1	1.64
PDHP26	75 / 50	60 / 62	6 / 5	3	11.0	0.841	15.3 / 33.9 / 55.9	1.79
PDHP28	60 / 60	50 / 52	6 / 6	9	5.2	0.825	17.8 / 37.9 / 63.2	1.74
PDHP29	60 / 180	50 / 52	6 / 3	9	5.2	0.616	5.4 / 11.4 / 20.0	3.37
PDHP27	60 / 180	50 / 55	6 / 5	9	10.2	0.809	13.3 / 27.8 / 47.7	2.27
PDHP30	60 / 180	50 / 58	6 / 8	9	15.1	0.84	16.9 / 31.5 / 50.7	1.93
PDHP31†	60 / 80	59 / 66	6 / 7.5	3	22.1	1.019	12.9 / 28.0 / 47.8	1.46
PDHP32†	60 / 80	59 / 67	6 / 7.5	3	22.1	0.925	14.5 / 32.0 / 55.5	1.58
PDHP33	63 / 70	60 / 67	6 / 8	3	22.0	1.048	19.5 / 41.3 / 70.2	1.36
PDHP34	71 / 71	60 / 65	9 / 8	3	22.2	0.885	40.1 / 78.0 / 119.1	0.83
PDHP35	60 / 70	55 / 61.5	5.5 / 8	3	22.1	0.908	20.0 / 42.6 / 67.6	1.68
PDHP36	70 / 70	60 / 66	7 / 8	3	22.1	0.753	12.8 / 28.3 / 58.1	1.90

Batch	Formic Acid addition rate (mL/min) / volume (mL)	Initial / Final Temperature (°C) *	Initial / Final Solution pH **	Volume (L)	Palladium Conc. (g/L)	Tap Density (g/cc)	Microtrac Particle Size d ₂₅ / d ₅₀ / d ₇₅ (µm)	BET Surface Area (m ² /g)
PDHP37	70 / 70	60 / 65.5	8 / 8	3	22.1	1.148	15.8 / 35.7 / 65.2	1.19
PDHP38	50 / 70	55 / 62	5 / 8	3	22.1	1.114	23.4 / 49.7 / 84.1	1.23
PDHP39‡	70 / 70	60 / 66	8 / 8	3	22.0	1.016	13.3 / 28.6 / 44.8	1.40
PDHP40	61 / 70	55 / 62	5 / 8	3	22.0	1.042	25.4 / 52.9 / 84.7	1.25
PDHP43	70 / 70	60 / 67	8 / 8	3	22.3	1.231	26.2 / 56.9 / 93.9	1.02
PDHP42	70 / 70	60 / 67	8 / 8	3	22.1	1.049	25.2 / 55.3 / 87.8	1.23
PDHP41†	70 / 70	60 / 67	8 / 8	3	22.1	0.784	17.3 / 39.5 / 61.8	1.91

* The final temperature is the highest temperature noted during the precipitation reaction (noncontinuous temperature monitoring).

** The final solution pH is that measured after the precipitation reaction was complete; in some cases, the pH increased later (decomposition of excess formic acid).

† The mixer was turned off for ~30 seconds during the precipitation reaction to minimize the amount of Pd and solution that was lost from the beaker (excessive reaction). PDHP32 was run at a slightly lower mixing rate, 1000 rpm, compared to the other batches in this category (1250 rpm).

‡ The mixer was turned off momentarily (5-10 seconds) during the precipitation reaction to minimize the amount of Pd and solution that was lost from the beaker.

|| The mixer speed was less than 1250 rpm (~500 rpm) initially during the precipitation reaction; at some point after the start of formic acid addition, the mixer speed was increased to 1250 rpm.

Figure 1. SEM photomicrographs of palladium processing batch PDHP18.

Figure 2. SEM photomicrographs of palladium processing batch PDHP24.

Figure 3. SEM photomicrographs of palladium processing batch PDHP37.

Tap Density = 1.0 g/cc
(fixed Pd/formic acid concentration)

Figure 4. Plot of the modeled addition rate, temperature, and pH reaction conditions required to produce palladium having a tap density of 1.0 g/cc, for a fixed palladium-to-formic acid concentration ratio.

Particle Size (d_{50})
(fixed Pd/formic acid concentration)

Figure 5. Plot of the modeled temperature and pH reaction conditions, and the resulting d_{50} particle size, for a fixed palladium-to-formic acid concentration ratio.

Figure 6. Plot of the modeled addition rate, temperature, and pH reaction conditions required to produce palladium having a surface area of 1.0 g/cc , for a fixed palladium-to-formic acid concentration ratio.

Appendix 1. Equipment and Components used in the Palladium Processing Project

Palladium Dissolution

hot plate - Precision Scientific Company (Chicago), catalog # 61725, 115V, 450W
hot plate - Thermolyne Nuova II hot plate / stirrer
1 L glass Erlenmeyer flask
250 mL graduated cylinder (for nitric acid addition)
0-100 μ L variable volume pipet and plastic pipet tips (for hydrochloric acid addition)
watch glass / rubber stopper(s)

Redwine Filtration (and Vinegar and Palladium Filtration)

2 L glass filter flask
filter holder - Micro Filtration Systems filter funnel (available from Cole-Parmer, catalog # E-02923-20)
filter paper - Micro Filtration Systems cellulose nitrate filter paper, 0.8 μ m pore, 47 mm diameter (Cole-Parmer, catalog # E-06645-34)
vacuum provided by water aspiration - tubing setup, with an in-line filter flask trap

Redwine Neutralization

4 L glass Erlenmeyer flask in a recirculator bath
Teflon-coated magnetic stir bar (1.5" L)
magnetic stirrer - Thermolyne Nuova II hot plate / stirrer
250 mL and 50 mL graduated cylinders (for ammonium hydroxide addition)
5 mL graduated cylinder (for acetic acid addition)
funnel
pH paper

Palladium Precipitation

4 L glass beaker or 4.5 gallon glass cylindrical jar in a recirculator bath
Masterflex tubing pump (Cole-Parmer model 7523-30 variable speed digital drive);
Masterflex L/S Easy-Load II pump head (Cole-Parmer, catalog # E-77201-60) and
L/S-25 tygon pump tubing (Cole-Parmer, catalog # E-06409-25)
Stir-Pak dual-shaft laboratory mixer and solid-state controller (Cole-Parmer, catalog # E-04554-10)
Fixed, dual-blade polypropylene paddle (Cole-Parmer, catalog # E-06367-10)
pH electrode (Cole-Parmer model 05992-20) and meter (Cole-Parmer model 05669-20)

Other Laboratory Equipment Used

Neslab Endocal RTE-4DD recirculator and Cole-Parmer Masterflex tubing pump (model WZ1R031 3200 rpm drive, model 7017-20 pump cartridge, and solid-state controller)
Plastic dishpan (~14" x 12" x 8" recirculator bath for 4 L glass flask and 4 L glass beaker) or
Rubbermaid 15.5 gallon plastic box (recirculator bath for 4.5 gallon cylindrical jar)
Mettler Gram-atic and Ohaus GT2100 analytical balances
Drying oven (Cole-Parmer model 5015-50)

Dessicators

100 mesh sieve (Spex Industries model 3536 small sieve set - 100, 200, 325, and 400 mesh nylon sieves and methacrylate cylinders)

Watch glasses - 8" (covers for 4 L beakers), 6" (for drying Pd precipitate), 3" (for drying filter paper used for redwine and vinegar filtration)

Ring stands, clamps, spatulas, tongs, forceps, thermometers, glass stir rods

Palladium Dissolution

Palladium is dissolved in nitric acid and hydrochloric acid in a 1 L Erlenmeyer flask, on a hot plate. In the photograph, the redwine solution is at room temperature.

Redwine Filtration

Redwine solution is vacuum-filtered using a 2 L filter flask, filter funnel, and 0.8 μm pore cellulose nitrate filter paper. Suction is provided by a water aspirator.

Redwine Neutralization

Redwine solution, in a 4 L glass Erlenmeyer flask in a 40 °C recirculating bath on top of a magnetic stirrer, is neutralized with ammonium hydroxide, and diluted with water. Acetic acid is added to the solution.

Palladium Precipitation

Palladium "vinegar" solution, in a 4 L glass beaker in a constant-temperature recirculating bath, is precipitated by adding formic acid using a tubing pump. The solution is stirred using a laboratory mixer, mounted in an off-center mixing configuration.

Manual shaking of 100 mesh sieve.

Appendix 2. Description and Tabulation of Reaction Conditions for Palladium Processing Batches PDHP17-43

Palladium processing batches PDHP17-24

These batches were made in a more systematic manner than the initial batches (PDHP1-16). A single variable in the processing conditions was changed, with the remainder of the conditions more consistent from batch-to-batch, although there were some minor differences in the individual batches.

Palladium was precipitated using formic acid in a stirred, glass reaction vessel. A laboratory mixer (Cole-Parmer Stir-Pak mixer model 4554-10) with a polypropylene, fixed dual-blade paddle assembly was mounted in an off-center mixing configuration in a 4 L glass beaker. The palladium concentration was approximately 22 g/L (65-67 grams of Pd dissolved in a 3 L volume of vinegar solution).

For batches PDHP17, 18, 19, and 20, the formic acid delivery rate was varied (20, 40, 60, and 77 mL/min, respectively). The initial solution pH for all four of these batches was nominally 6, and the initial temperature was nominally 60 °C. The incubation time (the time between the start of formic acid delivery and the time that the solution was observed to “go black”) was 15 seconds or less for all four of these batches. After addition of the formic acid, the final solution pH was ~8, and the solution temperature was approximately 64 °C. For batches PDHP17, 18, and 19, a decreasing amount of “bright” Pd formed, with the form changing from small flakes of bright Pd to small specks. For PDHP20, a slightly larger amount of bright Pd specks formed than for PDHP19. (The Pd precipitation reaction for batches 17-19 was done on consecutive days; batch 20 was done 11 days later, along with batches 21 and 22.)

Batches PDHP21 and 22 were made at a lower temperature than the 60 °C value used for PDHP17-20. The initial solution temperature for PDHP21 was 40 °C, and that for PDHP22 was 50 °C. The initial solution pH for these two batches was nominally 6, and the formic acid delivery rate was 60 mL/min. Therefore, batches PDHP21, 22, and 19 form a group for which the processing conditions were similar, except for the difference in solution temperature. For PDHP21, formic acid addition was completed before the precipitation reaction started. Formic acid was added for 80 seconds; 4 minutes after formic acid addition started, the solution temperature was 42 °C and the pH was ~3; 8 minutes after formic acid addition started, the solution began bubbling vigorously and continued doing so for approximately 3.5 minutes; the solution temperature increased to 49 °C, and the final solution pH was ~8. Very little bright Pd (specks) formed in this batch; the Pd precipitate was slightly darker black in color than that observed for the other batches (17-20 and 22). For PDHP22, the precipitation reaction started during the addition of formic acid. Formic acid was added for 80 seconds; 25 seconds after formic acid addition started, the solution turned black; 45 seconds after formic acid addition started, the solution began bubbling vigorously. The solution temperature after the reaction was complete was 56 °C, and the final solution pH was ~8. Some small flakes of bright Pd formed in this batch (more bright Pd formed in this batch than in batches 19 or 21).

The initial solution pH was varied for batches PDHP23 (pH 9) and 24 (pH 3). The precipitation reaction was done at 60 °C, with a formic acid addition rate of 60 mL/min.

Therefore, batches PDHP23, 24, and 19 form a group for which the processing conditions were similar, except for the difference in initial solution pH. For batch PDHP23, formic acid was added for 80 seconds; 42 seconds after formic acid addition started, the solution turned black; 70 seconds after formic acid addition started, the solution began bubbling vigorously and continued doing so for about 1 minute. The solution temperature after the reaction was complete was 65 °C, and the pH was ~8. Some fuming (acid-base reaction) was noted when the formic acid addition began. Some small flakes of bright Pd formed in this batch.

For batch PDHP24, formic acid was added for approximately 85 seconds; about 30 seconds after formic acid addition started, the solution began getting darker in color, gradually, but there was no obvious sharp transition when the solution “went black”; 2 minutes after formic acid addition started, the solution began bubbling very vigorously (excessively), and some of the solution and Pd precipitate was lost out the top of the beaker (into the recirculator bath). The mixer was turned off, and the reaction slowed (no more solution and precipitate out the top of the beaker); the solution temperature measured was 65 °C, and the solution pH was ~7. After the precipitation reaction was complete, the solution continued to bubble (decomposition of excess formic acid, presumably), and the pH increased to 8. Very little bright Pd (small flakes) formed - the majority of the precipitate was “very clean”. The Pd precipitate was slightly darker black in color than that observed for the other batches, darker than PDHP21. The mass of Pd precipitate and 100 mesh Pd tabulated below does not include ~1.2 g recovered from the recirculator bath and ~2 g of Pd not recovered.

Palladium processing batches PDHP25-30

Batch PDHP25 was intended to be a repeat of PDHP20; 22 g/L Pd, pH 6, 60 °C, 75 mL/min formic acid, 3 L volume (4 L glass beaker). The precipitation reaction for PDHP25 proceeded differently than that for PDHP20, however. Formic acid was added for 65 seconds at a rate of 75 mL/min; about 30 seconds after formic acid addition started, the solution began getting darker in color, gradually (no sharp transition); 2 minutes after formic acid addition started, the solution began bubbling; 3.5 minutes after formic acid addition started, the mixer was turned off for about 30 seconds to prevent some of the reaction mixture from being lost out the top of the beaker; 6 minutes after formic acid addition started, the solution temperature was 66 °C and the pH was ~7.5. A relatively large amount (but less than 5 g) of bright Pd formed on the walls of the beaker.

PDHP26 is a “Pd dilution” batch; 11 g/L Pd, pH 6, 60 °C, 75 mL/min formic acid, 3 L volume (4 L glass beaker). “Reprocess” means the starting material is bright Pd and Pd black from previous batches, not sponge. Note that the reagent volumes have also been decreased by a factor of ~2. Formic acid was added for 40 seconds and the solution began getting darker in color, gradually (no sharp transition); after addition, the solution temperature was 60 °C and the pH was ~2; 2 minutes after formic acid addition started, the solution began bubbling and continued doing so for a number of minutes. After the precipitation reaction was complete, the solution temperature was 62 °C and the pH was ~5; the solution continued bubbling (decomposition of excess formic acid) for a number of hours. The next day the solution pH was ~7.5. A small amount of bright Pd formed in this batch.

PDHP28, 29, 27, and 30 are “dilution batches”; approximately 5, 5, 10, and 15 g/L Pd, 9 L volume (4.5 gal. glass jar), with the Pd precipitation done at 50° C, initial solution pH 6, and a

formic acid addition rate of 60 mL/min. The HNO_3 , HCl , NH_4OH , and CH_3COOH reagent volumes are approximately the same for all these batches. For PDHP28 and 29, the Pd concentration is the same, but the formic acid concentration varies (60 mL formic acid for batch 28, 180 mL for batch 29). For PDHP28, formic acid was added for 1 minute, and the solution began getting darker in color, gradually (no sharp transition); after addition, the solution temperature was 50 °C and the pH was ~3; 10 minutes after formic acid addition started, the solution was still “just a black solution”; 12 minutes after formic acid addition started, the solution began bubbling and continued doing so for a number of minutes; 20 minutes after formic acid addition started, the solution temperature was 52 °C and the pH was ~6. After the precipitation reaction was complete, a small amount of bubbling in solution was observed (decomposition of excess formic acid). The solution pH measured the next day was 7. A small amount of bright Pd specks formed in this batch.

For PDHP29 (~5 g/L Pd), formic acid was added for 3 minutes, and the solution began getting darker in color gradually; after addition, the solution was a pH ~2, 50 °C, black-colored solution; 5 minutes after formic acid addition started, the solution began bubbling (more vigorously than that observed for PDHP28); 8 minutes after formic acid addition started, the solution temperature was 52 °C and the pH was ~3. After the precipitation reaction was complete, the solution pH was ~3 and a relatively large amount of bubbling in solution was observed (decomposition of excess formic acid). The solution was still bubbling the next day (20 hours after precipitation) and the pH was ~3. A very small amount of bright Pd specks formed in this batch; it's one of the “cleaner” batches.

For PDHP27 (~10 g/L Pd), formic acid was added for 3 minutes, and the solution began getting darker in color gradually; after addition, the solution was pH ~2, 50 °C, and black colored; 4.5 minutes after formic acid addition started, the solution began bubbling (more vigorously than that for PDHP29); 10 minutes after formic acid addition started, the solution temperature was 55 °C and the pH was ~5. After the precipitation reaction was complete, the solution pH was ~5 and a relatively large amount of bubbling in solution was observed. The solution was still bubbling the next day (20 hours after precipitation) and the pH was ~5. A small amount of bright Pd formed in this batch (more than that for PDHP29).

For PDHP30 (~15 g/L Pd), formic acid was added for 3 minutes, and the solution began getting darker in color gradually; after addition, the solution was pH ~2, 50 °C, and black colored; about 3.5 minutes after formic acid addition started, the solution began bubbling; 10 minutes after formic acid addition started, the solution temperature was 58 °C and the pH was ~7.5. After the precipitation reaction was complete, a small amount of bubbling in solution was observed and the pH was ~8. The next day (12 hours after precipitation), a small amount of bubbling in solution was observed and the pH was ~8. A small amount of bright Pd formed in this batch. (The starting material for PDHP30 was about half (0.47) sponge and about half Pd black and bright Pd from previous batches.)

Palladium processing batches PDHP31-38

Batch PDHP31 was intended to be a repeat of PDHP19; 22 g/L Pd, pH 6, 60 °C, 60 mL/min formic acid, 3 L volume (4 L glass beaker). The precipitation reaction for PDHP31 proceeded differently than that for PDHP19, however [larger volume of formic acid added to PDHP31 compared to PDHP19]. Formic acid was added for 80 seconds; the solution was black-colored before the formic acid addition was complete; 1.75 minutes after formic acid

addition started, the solution was pH ~2, 59 °C, and started bubbling. About 3 minutes after formic acid addition started, the mixer was turned off for ~30 seconds to minimize the amount of Pd and solution lost out the top of the beaker. Five minutes after formic acid addition started, the temperature was 66 °C and the pH was ~7. After the precipitation reaction was complete, the solution pH was ~7.5 and a small amount of bubbling in solution was observed. A relatively large amount of bright Pd formed, coating the majority of the inside of the beaker (~0.35 g coating of Pd).

PDHP32 was done using the same reaction conditions as those for PDHP31, except that the mixing speed was decreased to 1000 rpm, to see if a lower mixing speed would prevent the reaction from going too excessively fast. Formic acid was added for 80 seconds; the solution was black-colored before the formic acid addition was complete; 1.75 minutes after formic acid addition started, the solution was pH ~2, 59 °C, and started bubbling. About 4 minutes after formic acid addition started, the mixer was turned off for ~15 seconds to minimize the amount of Pd and solution lost out the top of the beaker; the temperature was 67 °C and the pH was ~6. After the precipitation reaction was complete, the solution pH was ~7.5 and a small amount of bubbling in solution was observed. A small amount of bright Pd formed in this batch.

PDHP33 was done for one set of “optimized” conditions: 63 mL/min formic acid addition rate, 60 °C, pH 6, 22 g/L Pd. Formic acid was added for 67 seconds; the solution was black-colored before the formic acid addition was complete; 1.75 minutes after formic acid addition started, the solution was pH ~2, 60 °C, and started bubbling. The solution bubbled vigorously for about 2.5 minutes, but the mixer did not have to be turned off during the precipitation reaction; the highest temperature measured was 67 °C. After the precipitation reaction was complete, the solution pH was ~8. A relatively large amount of bright Pd formed, coating the majority of the inside of the beaker (~0.9 g coating of Pd).

PDHP34 was done for a different set of “optimized” conditions: pH 9, 71 mL/min formic acid addition rate, 60 °C, 22 g/L Pd. Formic acid was added for 1 minute, and some fuming (acid-base reaction) was noted initially; the solution was black-colored before the formic acid addition was complete. About 1.6 minutes after formic acid addition started, the solution was pH ~3, 62 °C (? increased from acid-base reaction), and started bubbling. About 5 minutes after formic acid addition started, the temperature was 65 °C and the pH was ~8. A small amount of bright Pd (specks) formed in this batch. A relatively large amount of Pd black did not pass through the 100 mesh sieve (? large particle size).

PDHP35 was done for a different set of “optimized” conditions: pH 5.5, 60 mL/min formic acid addition rate, 55 °C, 22 g/L Pd. Formic acid was added for 70 seconds; the solution was black-colored before the formic acid addition was complete. About 2.1 minutes after formic acid addition began, the solution was pH ~2, 55 °C, and started bubbling; about 4.5 minutes after formic acid addition started, the solution was 61.5 °C, pH ~8, and stopped bubbling. A small amount of bright Pd (specks) formed in this batch.

PDHP36 was done for a different set of conditions (pH variation): pH 7, 70 mL/min formic acid addition rate, 60 °C, 22 g/L Pd. Formic acid was added for 1 minute; the solution was black-colored before the formic acid addition was complete. Less than 1 minute after formic acid addition started, the solution began bubbling; about 1.5 minutes after formic acid addition started, the bubbling stopped; 2.5 minutes after formic acid addition started, the solution was 66

°C and pH ~8. (This is the fastest precipitation reaction - usually the bubbling in solution persists 4-5 minutes after formic acid addition starts.) A relatively large amount of bright Pd formed, coating the majority of the inside of the beaker. This is the third successive batch, using this beaker, for which a significant bright Pd coating formed (batches PDHP31, 33, and 36); is it the beaker?

PDHP37 was done for a different set of conditions (pH variation): pH 8, 70 mL/min formic acid addition rate, 60 °C, 22 g/L Pd. Formic acid was added for 1 minute, and a small amount of fuming (acid-base reaction) was noted initially; the solution was black-colored before the formic acid addition was complete. About 1.4 minutes after formic acid addition started, the solution was pH ~2, 60.5 °C, and began bubbling; it continued bubbling for about 2.5 minutes. Five minutes after formic acid addition started, the solution was 65.5 °C and pH ~8. A relatively large amount of bright Pd formed, coating the majority of the inside of the beaker. (This beaker is a different "old" beaker that had been used for other Pd batches, not the one used for PDHP31, 33, and 36.)

PDHP38 was done for a different set of conditions (pH variation): pH 5, 50 mL/min formic acid addition rate, 55 °C, 22 g/L Pd. Formic acid was added for 1.4 minutes; the solution was black-colored before the formic acid addition was complete. Approximately 2.6 minutes after formic acid addition started, the solution was pH ~2, 55 °C, and began bubbling; it continued bubbling for about 4 minutes. At 6.5 minutes after formic acid addition started, the temperature was 62 °C; the final solution pH was ~8. A small amount of bright Pd (specks) formed in this batch; no bright Pd coating formed on the walls of the new beaker used.

Palladium processing batches PDHP39-43

PDHP39 was a repeat of PDHP37 - pH 8, 70 mL/min formic acid addition rate, 60 °C, 22 g/L Pd. Formic acid was added for 1 minute, and a small amount of fuming (acid-base reaction) was noted initially; the solution was black-colored before the formic acid addition was complete. About 1.6 minutes after formic acid addition started, the solution was pH ~2, 60 °C, and began bubbling. About 3 minutes after formic acid addition started, the mixer was turned off momentarily (~5-10 seconds) to minimize the amount of Pd and solution lost out the top of the beaker. About 4.5 minutes after formic acid addition started, the solution was 66 °C, pH ~8, and stopped bubbling. A small amount of bright Pd (specks) formed in this batch; no bright Pd coating formed on the walls of the beaker used.

PDHP40 was a repeat of PDHP38 (pH 5, 55 °C, 22 g/L Pd), except that the formic acid addition rate was increased to 61 mL/min. Formic acid was added for 1.15 minutes; the solution was black-colored before the formic acid addition was complete. About 2.4 minutes after formic acid addition started, the solution was pH ~2, 55 °C, and began bubbling; it continued bubbling for about 5 minutes. At 6.5 minutes after formic acid addition started, the solution was 62 °C, pH ~8. A small amount of bright Pd (specks) formed in this batch; no bright Pd coating formed on the walls of the new beaker used.

PDHP43 was a repeat of PDHP37 - pH 8, 70 mL/min formic acid addition rate, 60 °C, 22 g/L Pd, done with Bob Malstrom. Formic acid was added for 1 minute; the solution was black-colored before the formic acid addition was complete. About 1.7 minutes after formic acid addition started, the solution began bubbling. Five minutes after formic acid addition started, the solution was 67 °C, which was the highest temperature noted during the precipitation reaction. The final solution pH was ~8 (pH 8.49 measured prior to Pd filtration). A small amount of

bright Pd (specks) formed in this batch; no bright Pd coating formed on the walls of the beaker used. The mass of Pd precipitate tabulated below includes 1.96 g of Pd scraped off the polypropylene mixer paddle; however, this Pd was not added to the rest of the Pd precipitate. [The mixer speed was less than 1250 rpm initially during the precipitation reaction; at some point (? after the 1-minute addition of formic acid), the mixer speed was increased to 1250 rpm. This batch appears to have a very low tap density and very large particles; a large amount (~30 grams) of this batch did not pass through the 100 mesh sieve.]

PDHP42 was a repeat of PDHP37 - pH 8, 70 mL/min formic acid addition rate, 60 °C, 22 g/L Pd, done with Bob Malstrom. For this batch (unlike the previous batches), the tygon pump tubing used to deliver formic acid was completely filled with formic acid before the start of the precipitation reaction; the pump was turned on to deliver formic acid to the solution and turned off after 1 minute. After the precipitation reaction was complete, the formic acid remaining in the tygon pump tubing was pumped into a small waster container. About 0.5 minutes after formic acid addition started, the solution was black-colored; 1.5 minutes after formic acid addition started, the solution began bubbling. Four minutes after formic acid addition started, the solution was pH ~6, 66 °C, and the bubbling in solution decreased dramatically; 5 minutes after formic acid addition started, the solution was pH ~8, 67 °C, and a small amount of bubbling in solution was observed. The final solution pH was ~8 (pH 8.25 measured prior to Pd filtration). A very small amount of bright Pd (specks) formed in this batch, less than that formed in batch PDHP43; PDHP42 is one of the “cleanest” batches. No bright Pd coating formed on the walls of the beaker used. The mass of Pd precipitate tabulated below includes 1.67 g of Pd scraped off the polypropylene mixer paddle; however, this Pd was not added to the rest of the Pd precipitate.

PDHP41 was a repeat of PDHP37 - pH 8, 70 mL/min formic acid addition rate, 60 °C, 22 g/L Pd. For this batch, the tygon pump tubing used to deliver formic acid was completely filled with formic acid before the start of the precipitation reaction, as was done for batch PDHP42. Formic acid was added for 1 minute; about 0.5 minutes after formic acid addition started, the solution was black-colored. At 1.6 minutes after formic acid addition started, the solution began bubbling; about 2.5 minutes after formic acid addition started, the mixer was turned off for ~30 seconds to minimize the amount of Pd and solution that was lost out the top of the beaker. At 4 minutes after formic acid addition started, the bubbling in solution had decreased dramatically, and the solution was 67 °C and pH ~8. The final solution pH was ~8 (pH 8.13 measured prior to Pd filtration). A very small amount of bright Pd (specks) formed in this batch, comparable to the amount formed in batch PDHP42; PDHP41 is one of the “cleanest” batches. No bright Pd coating formed on the walls of the beaker used. The mass of Pd precipitate tabulated below includes 1.80 g of Pd scraped off the polypropylene mixer paddle; however, this Pd was not added to the rest of the Pd precipitate.

Batch	PDHP17	PDHP18	PDHP19	PDHP20	PDHP21
Pd sponge (g)	67.66	66.67	66.52	67.30	67.31
HNO ₃ (mL)	350	350	350	350	350
HCl (μL)	70	70	70	70	70
H ₂ O ₂ (mL)	-	-	100	-	-
Undissolved Pd (g)	0.3	1.92	0.42	0.013	0.035
Dissolved Pd (g)	67.36	64.75	66.1	67.28	67.27
Redwine (L)	1.1	1.2	1.0	1.2	1.0
NH ₄ OH (mL)	450	450	450	400	400
CH ₃ COOH (mL)	4.3	4.3	4.4	4.4	4.4
water (mL)					
Fe ₂ O ₃ (g)	0.0097	0.15 *	0.0143	2.15 *	0.007
HNO ₃ (mL)	45	80	60	50	30
NH ₄ OH (mL)					10
Vinegar (L)	3	3	3	3	3
Solution pH	6	6	6	6	6
Temperature (°C)	59	59	58	59	40
Pd Concentration (g/L)	22.5	21.6	22.0	22.4	22.4
HCOOH Addition rate (mL/min)	20	40	60	77	60
HCOOH volume (mL)	66.7	66.7	70	77	80
Incubation time (min)	0.25	~0.17	<0.25	<0.25	8 (bubbling)
Mixing method	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer
Mixing rate	1250 rpm	1250 rpm	1250 rpm	1250 rpm	1250 rpm
Container	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr
Pd precipitate (g)	67.56	65.07	66.20	65.98	67.59
100 mesh Pd (g)	55.50	58.57	63.70	60.55	63.47
Tap density (g/cc)	1.696	1.611	1.491	0.975	0.794
Microtrac Size					
d ₂₅ (μm) [10-26]	17.14	11.30	12.27	12.27	36.85
d ₅₀ (μm) [21-47]	35.37	26.88	25.82	23.63	60.70
d ₇₅ (μm) [30-67]	70.19	55.01	54.12	44.54	86.73
BETsurface area (m ² /g)	0.633	0.767	0.7553	1.2216	1.852

Batch	PDHP22	PDHP23	PDHP24	PDHP25	PDHP26
					Reprocess
Pd sponge (g)	67.16	66.33	66.41	64.91	33.09
HNO ₃ (mL)	350	350	350	350	175
HCl (μL)	70	70	70	70	35
H ₂ O ₂ (mL)	-	-	-	-	-
Undissolved Pd (g)	0.035	0.021	0.01	0	0
Dissolved Pd (g)	67.12	66.31	66.40	64.91	33.09
Redwine (L)	1.0	1.1	1.1	1.1	1.1
NH ₄ OH (mL)	420	440	440	430	220
CH ₃ COOH (mL)	4.4	4.4	4.4	4.3	2.3
water (mL)					
Fe ₂ O ₃ (g)	0.049 *	0.023 *	0.005	0.005	0
HNO ₃ (mL)	42	-	62	30	20
NH ₄ OH (mL)			3		
Vinegar (L)	3	3	3	3	3
Solution pH	6	9	3	6	6
Temperature (°C)	50	60	60	60	60
Pd Concentration (g/L)	22.4	22.1	22.1	21.6	11.0
HCOOH Addition rate (mL/min)	60	60	60	75	75
HCOOH volume (mL)	80	80	85	81	50
Incubation time (min)	0.42	0.7	2	2	2
			(bubbling)	(bubbling)	(bubbling)
Mixing method	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer
Mixing rate	1250 rpm	1250 rpm	1250 rpm	1250 rpm	1250 rpm
Container	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr
Pd precipitate (g)	67.09	66.37	63.16	65.15	32.81
100 mesh Pd (g)	63.85	58.50	61.79	58.81	30.18
Tap density (g/cc)	1.062	1.142	0.65	1.076	0.841
Microtrac Size					
d ₂₅ (μm) [10-26]	20.19	21.57	14.60	14.8	15.3
d ₅₀ (μm) [21-47]	34.57	40.06	33.58	34.8	33.9
d ₇₅ (μm) [30-67]	53.43	68.89	55.35	61.1	55.9
BETsurface area (m ² /g)	0.7852	0.6972	2.6915	1.64	1.79

Batch	PDHP28	PDHP29	PDHP27	PDHP30	
				~½ Reprocess	
Pd sponge (g)	46.49	46.46	92.13	136.46	
HNO ₃ (mL)	350	350	350	350	
HCl (μL)	70	70	70	70	
Undissolved Pd (g)	0	0	0.02	0.44	
Dissolved Pd (g)	46.49	46.46	92.11	136.02	
Redwine (L)	1	1.1	1	1.2	
NH ₄ OH (mL)	430	420	440	480	
CH ₃ COOH (mL)	4.3	4.2	4.3	4.5	
water (mL)					
Fe ₂ O ₃ (g)	0.001	0.003	0.007	0.027 *	
HNO ₃ (mL)	35	40	30	43	
NH ₄ OH (mL)	-	-	-	-	
Vinegar (L)	9	9	9	9	
Solution pH	6	6	6	6	
Temperature (°C)	50	50	50	50	
Pd Concentration (g/L)	5.2	5.2	10.2	15.1	
HCOOH Addition rate (mL/min)	60	60	60	60	
HCOOH volume (mL)	60	180	180	180	
Incubation time (min)	12 (bubbling)	5 (bubbling)	4.5 (bubbling)	3.5 (bubbling)	
Mixing method	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer	
Mixing rate	1500 rpm	1500 rpm	1500 rpm	1500 rpm	
Container	4.5gal Gl.Jar	4.5gal Gl.Jar	4.5gal Gl.Jar	4.5gal Gl.Jar	
Pd precipitate (g)	46.71	46.63	92.76	136.50	
100 mesh Pd (g)	43.34	45.49	88.23	127.46	
Tap density (g/cc)	0.825	0.616	0.809	0.84	
Microtrac Size					
d ₂₅ (μm) [10-26]	17.8	5.4	13.3	16.9	
d ₅₀ (μm) [21-47]	37.9	11.4	27.8	31.5	
d ₇₅ (μm) [30-67]	63.2	20.0	47.7	50.7	
BETsurface area (m ² /g)	1.74	3.37	2.27	1.93	

Batch	PDHP31	PDHP32	PDHP33	PDHP34	PDHP35
	Reprocess	Reprocess	Reprocess	Reprocess	Reprocess
Pd sponge (g)	66.38	66.15	66.14	66.49	66.20
HNO ₃ (mL)	350	350	350	350	350
HCl (μL)	70	70	70	70	70
Undissolved Pd (g)	0	0	0	0	0
Dissolved Pd (g)	66.38	66.15	66.14	66.49	66.20
Redwine (L)	1	1	1	1	1
NH ₄ OH (mL)	430	430	430	430	430
CH ₃ COOH (mL)	4.3	4.3	4.3	4.3	4.3
water (mL)					
Fe ₂ O ₃ (g)	0	0	0	0	0.001
HNO ₃ (mL)	29	34	30	-	28
NH ₄ OH (mL)	a few drops	~1	-	37	2
Vinegar (L)	3	3	3	3	3
Solution pH	6	6	6	9	5.5
Temperature (°C)	59	59	60	60	55
Pd Concentration (g/L)	22.1	22.1	22.0	22.2	22.1
HCOOH Addition rate (mL/min)	60	60	63	71	60
HCOOH volume (mL)	80	80	70	71	70
Incubation time (min)	~0.5; 1.75 (bubbling)	~0.5; 1.75 (bubbling)	~0.5; 1.75 (bubbling)	~0.5; 1.6 (bubbling)	~0.5; 2.1 (bubbling)
Mixing method	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer
Mixing rate	1250 rpm	1000 rpm	1250 rpm	1250 rpm	1250 rpm
Container	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr
Pd precipitate (g)	66.20	66.23	64.86	66.50	66.33
100 mesh Pd (g)	60.05	61.63	58.40	53.50	62.21
Tap density (g/cc)	1.019	0.925	1.048	0.885	0.908
Microtrac Size					
d ₂₅ (μm) [10-26]	12.9	14.5	19.5	40.1	20.0
d ₅₀ (μm) [21-47]	28.0	32.0	41.3	78.0	42.6
d ₇₅ (μm) [30-67]	47.8	55.5	70.2	119.1	67.6
BETsurface area (m ² /g)	1.46	1.58	1.36	0.83	1.68

Batch	PDHP36	PDHP37	PDHP38	PDHP39	PDHP40
	Reprocess	Reprocess	Reprocess	Reprocess	Reprocess
Pd sponge (g)	66.19	66.20	66.25	66.14	66.13
HNO ₃ (mL)	350	350	350	350	350
HCl (μL)	70	70	70	70	70
Undissolved Pd (g)	0	0.02	0	0	0
Dissolved Pd (g)	66.19	66.18	66.25	66.14	66.13
Redwine (L)	1	1	1	1	1
NH ₄ OH (mL)	430	430	430	430	430
CH ₃ COOH (mL)	4.3	4.3	4.3	4.3	4.4
water (mL)					
Fe ₂ O ₃ (g)	0.002	0	0	0.001	0
HNO ₃ (mL)	31	22	36	18	31
NH ₄ OH (mL)	-	-	1	3	-
Vinegar (L)	3	3	3	3	3
Solution pH	7	8	5	8	5
Temperature (°C)	60	60	55	60	55
Pd Concentration (g/L)	22.1	22.1	22.1	22.0	22.0
HCOOH Addition rate (mL/min)	70	70	50	70	61
HCOOH volume (mL)	70	70	70	70	70
Incubation time (min)	~0.5; 0.8 (bubbling)	~0.5; 1.4 (bubbling)	~0.5; 2.6 (bubbling)	~0.5; 1.6 (bubbling)	~0.5; 2.4 (bubbling)
Mixing method	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer	off-c Mixer
Mixing rate	1250 rpm	1250 rpm	1250 rpm	1250 rpm	1250 rpm
Container	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr
Pd precipitate (g)	66.30	66.08	66.29	66.13	66.11
100 mesh Pd (g)	60.65	61.45	56.19	61.12	57.20
Tap density (g/cc)	0.753	1.148	1.114	1.016	1.042
Microtrac Size					
d ₂₅ (μm) [10-26]	12.8	15.8	23.4	13.3	25.4
d ₅₀ (μm) [21-47]	28.3	35.7	49.7	28.6	52.9
d ₇₅ (μm) [30-67]	58.1	65.2	84.1	44.8	84.7
BETsurface area (m ² /g)	1.90	1.19	1.23	1.40	1.25

Batch	PDHP41	PDHP42	PDHP43		
	Reprocess	Reprocess	Reprocess		
Pd sponge (g)	66.15	66.20	67.01		
HNO ₃ (mL)	350	350	350		
HCl (μL)	70	70	70		
Undissolved Pd (g)	0	0	0		
Dissolved Pd (g)	66.15	66.20	67.01		
Redwine (L)	1	~1	~1		
NH ₄ OH (mL)	430	430	430		
CH ₃ COOH (mL)	4.3	4.4	4.3		
water (mL)					
Fe ₂ O ₃ (g)	0.001	0	0		
HNO ₃ (mL)	13	17	-		
NH ₄ OH (mL)	-	-	-		
Vinegar (L)	3	3	3		
Solution pH	8	8	8		
Temperature (°C)	60	60	60		
Pd Concentration (g/L)	22.1	22.1	22.3		
HCOOH Addition rate (mL/min)	70	70	70		
HCOOH volume (mL)	70	70	70		
Incubation time (min)	~0.5; 1.6 (bubbling)	~0.5; 1.5 (bubbling)	~0.5; 1.7 (bubbling)		
Mixing method	off-c Mixer	off-c Mixer	off-c Mixer		
Mixing rate	1250 rpm	1250 rpm	*1250 rpm*		
Container	4L Gl.Beakr	4L Gl.Beakr	4L Gl.Beakr		
Pd precipitate (g)	66.05	66.09	67.05		
100 mesh Pd (g)	61.21	61.02	37.54		
Tap density (g/cc)	0.784	1.049	1.231		
Microtrac Size					
d ₂₅ (μm) [10-26]	17.3	25.2	26.2		
d ₅₀ (μm) [21-47]	39.5	55.3	56.9		
d ₇₅ (μm) [30-67]	61.8	87.8	93.9		
BETsurface area (m ² /g)	1.91	1.23	1.02		