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Hydrous Melt Catalyst Synthesis

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Hydrous melts of stannous chloride are convenient solvents for the preparation of tin–palladium electroless plating catalysts. Pure melts of stannous chloride rapidly reduce palladium halides to a noncatalytic state. The addition of alkali halides greatly modifies this reaction to give stable catalytic species. The solidified melt dissolves readily in dilute HCl. This solution is highly active as a catalyst for electroless plating of nonconductors.

INTRODUCTION

Electroless plating is a surface-coating technique which involves the autocatalytic reduction of a dissolved metal salt by a dissolved reducing agent at an interface to form a continuous film. Electroless nickel and electroless copper are the most familiar examples. Commercially usable baths must be stabilized so that no bulk decomposition or container-initiated decomposition occurs. Dielectrics such as plastics are not platable by such baths unless they are first coated with a catalyst.

The present catalyst which is almost universally used is the reaction product of stannous and palladium chlorides (*1*). Nonconductors are coated with the catalyst by immersion in a hydrochloric acid solution of the tin–palladium reaction product. This catalyst is an unusual example of a "throw-away" precious metal catalyst because it is used once and never recovered. Over 20 × 10^6 m^2 of printed circuit boards and platable plastics are coated with this catalyst yearly. Its high activity at very low concentrations ($<5 \times 10^{-6}$ g $PdCl_2/cm^2$) make this economically feasible.

A large number of patents have been issued on this type of catalyst, most of which pertain to preparation of a stabilized acidic liquid concentrate (*1–23*). These tin–palladium catalysts are formed by reacting specific ratios of the two materials in an aqueous acidic solution, normally hydrochloric acid. A large number of chemicals have been used to modify various properties of the catalyst. Liquid concentrates do not have unlimited shelf life since palladium slowly precipitates during storage.

The reaction of stannous and palladium chlorides in acid solution has been studied extensively (*24–31*). At low ratios of tin to palladium (<2/1), the reduction goes to completion very rapidly (Fig. 1). At higher ratios, the reaction slows down dramatically and a number of color phases can be identified by spectrophotometry. Some of these intermediate colors are doubtless due to successive substitution and isomerization of $SnCl_3^-$ on $PdCl_4^{2-}$ as has been shown for the platinum system (*32–33*). However, all of these complexes have not yet been isolated due to their extreme lability. Metallic palladium and/or palladium/tin alloys are the end product of the reduction.

The active plating catalyst is the red-brown solution, which can be stable for long periods. The other color phases also exhibit some catalytic activity, but cannot be stabilized easily. The colloidal brown suspension has poor catalytic activity.

The actual catalyst species has been described as a colloid, a complex, and a

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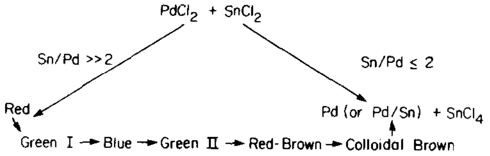

FIG. 1. The reduction of $PdCl_2$ by $SnCl_2$ can show a number of colors in both aqueous acid, nonaqueous solvents, and hydrous melts, depending largely on the ratios of the reactants.

mixture (*1, 2, 6, 7, 13, 24–30, 34–37*). Various structures have been described for the complex. The colloid has been said to be Pd or Pd/Sn alloy, surrounded by a coating of tin compounds. Regardless of the actual structure of the electroless plating catalyst, it can be conveniently characterized by simple tests for activity. The two most important factors are the ability to absorb onto dielectric surfaces and to efficiently initiate electroless plating.

Recently several patents have appeared on the preparation of a solid catalyst concentrate (*34–37*). These patents are similar to earlier patents, as the catalyst is prepared in the same manner by reaction in acid solution. The excess water and acid are then removed by evaporation. Solid catalysts are safer to handle and store and have longer shelf lives than liquid catalysts. They are easily dissolved in dilute acid for use.

A new catalyst synthesis procedure has been developed which directly gives a solid catalyst concentrate (*38–39*). Hydrated stannous chloride melts of variable composition have been found to be completely effective for production of a tin–palladium electroless plating catalyst. A unique feature of this process is that no extrinsic source of acid is necessary. While acids may be used in this process, they are easily replaced by water-soluble halide salts. This method may also be useful for the preparation of a variety of precious metal–tin complexes.

Most hydrated inorganic salts lose water of hydration on heating but do not melt. However, a number will dissolve in their own water of hydration to give hydrous melts. Stannous chloride dihydrate provides a convenient melt due to its low melting point (37.7°C), its reducing character, and its ability to form melts over a wide range of water contents. It is also a good solvent system for many other inorganic salts, including alkali halides and precious metal compounds.

Hydrous stannous melts have been the subject of intensive catalyst research, some of which will be reported here. The melts are interesting because of their tin content (>12 M/liter), high acidity, ease of use compared to anhydrous molten salts, and ease of variation of solidification temperatures, melt, fluidities, chemical activity, etc. Hydrous stannous chloride melts have been found to yield the same types of intermediate color phases with palladium chloride as have conventional aqueous acid solutions. The catalytic reaction product is at least as active as an electroless tin–palladium catalyst prepared in the conventional manner (*31, 38, 39*).

METHODS

All chemicals used were ACS reagent grade or better and were used without further purification. The $PdCl_2$ was from Englehard. All reactions were run under nitrogen to prevent oxidation. The constant-temperature water bath was maintained at ±2°C during the reactions. Vigorous mixing was assured with a mechanical agitator. A condenser was used to ensure constant water content of the melt.

Catalyst absorption was measured with 150-cm^2 test panels of EPB-3570 acrylonitrile–butadiene–styrene plastic (Borg–Warner Cycolac). All panels were processed with the standard electroless plating system described in Table 1. Panels used for absorption measurements were rinsed and dried after immersion in the catalyst test bath. All catalyst baths were 3.0 ± 0.1 N HCl at 25 ± 1°C.

Catalyst absorption was measured by

TABLE 1

Processing Conditions

Step[a]	Description	Temperature (°C)	Time (min)
E-22 etch[b]	CrO_3–H_2SO_4–H_2O	65	8
D-270 neutralizer[b]	Acidic Cr^{6+} reducing agent	25	1
Catalyst	As per text	25	5
Accelerator	10% HCl	50	1
N-35 electroless nickel[b]	Alkaline nickel-hypophosphite	25	6

[a] Thorough water rinse after each step.

[b] Borg–Warner Chemicals electroless plating solutions.

stripping each test panel in 50 ml of boiling 3 *N* HCl containing 2 ml of 30% H_2O_2 for 5 min. Palladium and tin analyses were done by atomic absorption.

Oxidation rates were measured using paired photocells and timers. A 250-ml 3 *N* HCl sample of each test solution was placed in a 500-ml graduated cylinder. Compressed air was bubbled through a coarse glass frit dispersion tube at approximately 1200 ml/min. The original opaque reddish-brown color rapidly changes to translucent yellow as the last traces of stannous ion are oxidized. This transition activates the photocell to stop the timer. All test runs were paired with a master batch of commercial plating catalyst prepared to the same stannous ion concentration. Uniformity was better than ±10%.

RESULTS AND DISCUSSION

Anhydrous stannous chloride melts (>250°C) react instantly with salts such as $PdCl_2$ and K_2PdCl_4 to give metallic palladium. Addition of an alkali halide such as KCl to the melt before addition of the palladium salt has no beneficial effect. Such materials give no catalytic activity for electroless plating when dissolved in acid and tested.

Hydrous stannous chloride ($SnCl_2 \cdot 2H_2O$) melts react readily with $PdCl_2$ to give a reddish-brown melt which solidifies easily. This material is catalytically active when tested. However, the activity is low and very variable even though the catalyst solutions may appear the normal opaque reddish brown.

A stable, active catalyst resulted when any of a number of metal halides were added to the hydrous melt. Excellent results were obtained when a double salt such as K_2PdCl_4 was added to the hydrous melt, when a halide such as KCl was predissolved in the hydrous melt, or when an aqueous solution of KCl and $PdCl_2$ was added to a melt of stoichiometric or nonstoichiometric composition. A large number of salts were useful, including LiCl, NaCl, KCl, $CaCl_2$, $MgCl_2$, $NiCl_2$, $CrCl_3$, $LaCl_3$, NaBr, KBr, etc. Some halides did not work because they oxidized the stannous ions ($FeCl_3$), hydrolyzed in the melt ($AlCl_3$), poisoned the electroless reaction ($PbCl_2$), or gave an inactive catalyst ($ZnCl_2$).

The mechanism of action of the added metal halides is thought to be twofold. The excess halide suppresses the hydrolysis of the $SnCl_2$

$$SnCl_2 + H_2O \rightleftharpoons Sn(OH)Cl + HCl$$

in the melt. This hydrolysis is self-limiting in pure melts. The melts are clear but extremely acidic. $SnCl_2$ also forms a series of chloro (or other halide) complexes, SnX_n^{+2-n}, where $n = 0$–3. The added halide greatly increases the proportion of the desired $SnCl_3^-$ species.

This is in accord with the known chemistry of making aqueous tin–palladium catalyst solutions. HCl is the preferred acid as it both inhibits hydrolysis and increases the $SnCl_3^-$ concentration. H_2SO_4 and H_3PO_4 produce a poor quality tin–palladium catalyst unless a halide salt is added.

Separate experiments were also run using aqueous tin solutions which did not contain added acids. A concentrated alkali or alkaline earth chloride solution was prepared and 0.6 *M* $SnCl_2$ added per liter. A 5- to 10-*M* excess of the halide was needed to prevent tin hydrolysis and to prepare the tin–palladium catalyst. However, the concentrated solution had a relatively short storage life. The activity of this catalyst was tested both in 3 *N* HCl solution and in concentrated halide solution. In both cases, the catalyst activity was much inferior to the hydrous melt type of catalyst.

A large number of catalyst preparations were made to check the effects of many of the variables in this system. The tin–palladium reaction in aqueous solution is known to be influenced by the pH, halide concentration, absolute concentration of tin and palladium salts, ratio of tin to palladium, temperature, reaction time, and other factors. Many of these variables are not independent of each other. Most of the developmental work was done using the fractional factorial method (*40–43*). This allowed simultaneous variation of up to eight parameters, followed by iterative optimization steps.

The most important variables identified by the fractional factorial work were selected for further study. The ones presented here include the addition of $PdCl_2$ or K_2PdCl_4 to the melt, the ratio of Pd to Sn, the reaction temperature, the ratio of KCl to $PdCl_2$, and the use of a number of other halide salts in place of KCl.

Variation of Pd/Sn Ratio

The purpose of this run was to produce the catalytic species rapidly by using an initial Sn/Pd ratio of 4, and then dilute it with larger amounts of tin (Sn/Pd ratios of 16 and 64) to see if the product was stabilized. Two palladium salts were tested, $PdCl_2$ and K_2PdCl_4.

In the first series 1.9 g K_2PdCl_4 (0.0058 *M*) was added with vigorous agitation to a mixture of 2.7 g KCl (0.036 *M*) and 5.4 g $SnCl_2 \cdot 2H_2O$ (0.024 *M*) at 95°C. After 15 min, a sample of 0.6 g was removed (I) and a second addition of 15 g ($SnCl_2 \cdot 2H_2O$) was made. This sample had been preheated and was added as a melt at 95°C. After 5 min, an additional sample of 1.6 g was removed (II) and 56 g stannous chloride was added. The third sample of 5.6 g (III) was removed after 5 min.

An identical series was run using 1.03 g $PdCl_2$ (0.0058 *M*) added to a mixture of 3.6 g KCl (0.0048 *M*) and 5.4 g $SnCl_2 \cdot 2H_2O$ (0.024 *M*) at 95°C. The composition of this melt was exactly the same as the first, but all of the KCl was predissolved in the melt instead of partially being added as the double salt. Note that runs I and IV had such a small amount of $SnCl_2 \cdot 2H_2O$ relative to the added KCl that the reaction product was a paste; in other runs sufficient material was present to give a homogeneous melt.

Duplicate test panels were analyzed for absorbed palladium and tin; the results are given as $PdCl_2$ and $SnCl_4$ for convenience in Table 2.

The working catalyst baths prepared from these materials were not completely homogeneous. Some reduction occurred to give large particles which precipitate rapidly. This allows the general comparison of noncatalytically usable palladium which precipitates, and catalytic forms which may be colloidal or complexed which stay in solution. The working baths were prepared and allowed to stand for at least 1 hr before using to test catalytic activity. After use, and without stirring, a 20-ml sample of solution was removed from the top for analysis.

These data show that approximately 20% of the total palladium precipitated from the working bath when solid K_2PdCl_4 was the added complex. This compares with 40–60% precipitation when solid $PdCl_2$ is used directly. Comparable results have been seen with conventional liquid catalysts, as addition of a $PdCl_2$/HCl solution gives better results than addition of solid $PdCl_2$. This indicates that $SnCl_3^-$ may react much more slowly with $PdCl_4^{2-}$ than with $PdCl_2$, thus favoring complex formation instead of reduction.

It is also possible that the added halide moderates the reaction by increasing the amount of $SnCl_3^-$ relative to $SnCl_2$ and $SnCl^+$ in the melt. However, in runs I and IV, there were twice as many moles of KCl as moles of $SnCl_2$ present. Run IV with the

TABLE 2

Effect of Tin/Palladium Ratio

Run	Ratio Sn/Pd	Absorption (10^{-6} g/cm^2)		Working bath concentrations[a]	
		$PdCl_2$	$SnCl_4$	$PdCl_2$ (mg/liter)	Sn (M/liter)
K_2PdCl_2 addition					
I	4	2.6	4.4	194 (240)	0.0067 (0.0054)
II	16	2.8	5.1	199 (247)	0.025 (0.022)
III	64	1.6	4.4	198 (250)	0.092 (0.091)
$PdCl_2$ addition					
IV	4	1.1	7.3	149 (240)	0.0058 (0.0054)
V	16	0.8	5.8	116 (247)	0.023 (0.022)
VI	64	1.1	10.3	100 (250)	0.102 (0.091)

[a] Actual vs (theoretical) values.

$PdCl_2$ addition still showed much more palladium reduction. Other runs made with varying amounts of added KCl showed no trends; only the type of added palladium compound made a difference.

The working bath compositions I–III show that the effective palladium concentration does not change on dilution with excess $SnCl_2$ so the reduction was essentially quenched. The test panels show no great variation in absorbed tin as the concentration is changed by 16-fold, but it seems to reach a limiting value. The palladium concentration in the working bath varied from 25 to 1.5% of the tin. It is much more strongly absorbed than the tin species as the amounts absorbed are comparable to the tin absorption. Only at the highest tin ratio was there a decrease in palladium absorption, but the tin absorption remained fairly constant. A duplicate set of test panels from each run was processed through the electroless nickel bath. Nickel coverage was 100% in all three cases, showing that the amount and activity of the absorbed catalyst was sufficient.

Runs IV–VI were made with all the KCl present in the melt. The palladium was added as $PdCl_2$. In this case, palladium reduction continued even after additions of more stannous chloride. Tin absorption was greater and more variable, while palladium absorption was poorer. Even these levels of absorbed palladium are normally more than sufficient for catalytic activity as measured by surface coverage during plating. Plating results showed nickel coverages of 5 (IV), 80 (V), and 60% (VI). The conclusion is that much of the absorbed palladium is in the form of relatively large, low-surface-area colloids.

No particular correlation was seen between soluble palladium concentration and absorbed palladium. This is due to the relatively long (5-min) immersion time used. As the amount absorbed is an exponential function of the immersion time, great differences would only be visible with short immersions (*31*, *44–47*). The effect of any stannic ion present was ignored in this work; stannic content would have been low due to reaction under nitrogen, and relatively uniform due to identical treatment once exposed to air. Stannic species are known to increase catalyst absorption when independently varied (*5*, *12*, *23*, *45–49*).

Variation of Reaction Temperature

The reaction temperature is a major variable in this system. A two-step reaction was used which differed somewhat from that used in runs I–VI. The initial tin/palladium ratio was 2/1; after 15 min enough $SnCl_2 \cdot 2H_20$ was added to increase the ratio to 62/1. This type of two-step reaction is said to increase the activity of the final catalyst (*2*).

The syntheses were run using 1.8 g K_2PdCl_4 added to a paste of 2.8 g KCl and 2.5 g $SnCl_2 \cdot 2H_2O$, or 1.0 g $PdCl_2$ added to 3.6 g KCl and 2.5 g $SnCl_2 \cdot 2H_2O$. After 15 min reaction, a second addition of 76 g $SnCl_2 \cdot 2H_2O$ was made and the reaction continued for 15 min. Reaction temperatures were 60, 80, 95, and 110°C for the K_2PdCl_4 (VII–X) and $PdCl_2$ (XI–XIV) runs. The final catalyst was allowed to cool to a solid and tested as described earlier. The results are given in Table 3.

The moderating effect of K_2PdCl_4 vs $PdCl_2$ additions is clear. The K_2PdCl_4 addition showed much less reduction, as can be seen by the greater amounts of palladium in solution. Run VII showed no insoluble palladium, but this solution was distinctly green (Green II) showing that the reaction was incomplete. Catalysis was poorer for VII (90% nickel coverage) than for the higher-temperature reactions VIII–X (100% coverage). A trend was also seen with decreasing amounts of soluble palladium as the reaction temperature increased for runs VII–X.

Runs XI–XIV showed that $PdCl_2$ rapidly reacts to give large amounts of insoluble palladium. Only 30–35% of the palladium remained in solution at all temperatures used. This was true even for run XI, which still had the muddy green color typical of incompletely reacted solutions. The plating coverage was also poor. Eletroless nickel coverages were 25 (XI), 65 (XII), 65 (XIII), and 20% (XIV).

Variation of Added KCl

This set of reactions was done to see if there was an optimum amount of KCl for good activity. The previous results had shown that at constant added KCl, the K_2PdCl_4 salt addition gave much better results than $PdCl_2$. This implies that the equilibrium reaction with added chloride,

$$PdCl_2 + 2Cl^- \rightleftharpoons PdCl_4^{2-},$$

is slower than the reaction

$$PdCl_2 + SnCl_x^{2-x} \rightleftharpoons \text{(catalytic species or intermediates)}$$

with stannous chloride.

This series used a maximum of 20 moles of KCl dissolved in the $SnCl_2 \cdot 2H_2O$ melt per mole of $PdCl_2$. It is very possible that the reaction

TABLE 3

Effect of Reaction Temperature

Run	Temperature (°C)	Absorption (10^{-6} g/cm²)		Working bath concentrations[a]	
		$PdCl_2$	$SnCl_4$	$PdCl_2$ (mg/liter)	Sn (*M*/liter)
		K_2PdCl_4 addition			
VII	60	0.9	6.6	264 (249)[b]	0.089 (0.089)
VIII	80	1.1	7.3	176 (249)	0.088 (0.089)
IX	95	1.0	7.3	184 (249)	0.087 (0.089)
X	110	0.8	7.3	123 (249)	0.087 (0.089)
		$PdCl_2$ addition			
XI	60	0.3	5.1	73 (249)[b]	0.087 (0.089)
XII	80	0.3	5.1	88 (249)	0.087 (0.089)
XIII	95	0.6	5.1	85 (249)	0.087 (0.089)
XIV	110	0.6	5.1	76 (249)	0.087 (0.089)

[a] Actual vs (theoretical) values.

[b] Working bath muddy green instead of red-brown.

$$\mathrm{SnCl_2 + Cl^- \rightleftharpoons SnCl_3^-}$$

is the dominant one so that little free chloride would be available for complexation with $PdCl_2$. It was hoped that the experimental data would shed some light on this question.

It must be emphasized that no calculations of equilibria could be made in these systems; the appropriate data are completely lacking. These hydrous melts are extremely concentrated with $SnCl_2$ concentrations of around 12 *M*/liter. The water content of these melts is insufficient even to form a normal hydration shell around the species "in solution." A pure melt has only two water molecules per $SnCl_2$; run XXIV has only 1.5 moles of water per mole of $SnCl_2$ + KCl in the melt.

This set was run at 95°C for 15 min. A standard melt of 81 g (0.36 *M*) $SnCl_2 \cdot 2H_2O$ was used for each synthesis. The calculated amount of KCl was dissolved in it; then either K_2PdCl_4 or $PdCl_2$ was added. The first set used 1.8 g K_2PdCl_4 and 0 g (XV), 0.4 g (XVI), 0.8 g (XVII), 3.4 g (XVIII), and 7.6 g (XIX) KCl. The second set used 1.0 g $PdCl_2$ and 0.4 g (XX), 0.8 g (XXI), 1.7 g (XXII), 4.2 g (XXIII), and 8.4 g (XXIV) KCl. The ratios of excess chloride added to the melt relative to the $PdCl_2$ added varied from 1 to 20. Table 4 shows the results of varying the amounts of added chloride.

In every case, the K_2PdCl_4 addition gave a completely soluble catalyst, in contrast to the low and erratic results with $PdCl_2$. No trends of either palladium or tin absorption or of palladium reduction were seen over the range of added KCl used. The major effects of the KCl additions were in the plating coverage and in the physical form of the catalyst. Table 5 summarizes these data. The catalyst XX prepared with a 1 : 1 ratio of added halide to $PdCl_2$ exhibited almost no catalytic activity. This was surprising as both the amount of absorbed palladium on the test panels and the amount of soluble palladium in the working bath were similar to those in runs XXI–XXIV.

The most important factor is the influence of added halide on the final form of the catalyst. Catalysts such as XV and XX solidify rapidly to a hard friable solid. In contrast, XIX and XXIV give almost equal volume mixtures of transparent crystals and dark black liquid. The latter solutions show a large supercooling effect. In many cases, they can be kept in sealed

TABLE 4

Effect of KCl Variation

Run	$KCl/PdCl_2$ ratio	Absorption (10^{-6} g/cm^2)		Working bath concentrations[a]	
		$PdCl_2$	$SnCl_4$	$PdCl_2$ (mg/liter)	Sn (*M*/liter)
		K_2PdCl_4 addition			
XV	2/1	1.8	4.4	287 (246)	0.087 (0.089)
XVI	3/1	1.6	4.4	246 (248)	0.092 (0.089)
XVII	4/1	1.1	4.4	241 (249)	0.092 (0.089)
XVIII	10/1	1.3	4.4	249 (248)	0.092 (0.089)
XIX	20/1	1.3	7.3	241 (248)	0.087 (0.089)
		$PdCl_2$ addition			
XX	1/1	0.7	5.8	96 (247)	0.087 (0.089)
XXI	2/1	0.3	4.4	129 (248)	0.087 (0.089)
XXII	4/1	0.8	5.8	96 (248)	0.090 (0.089)
XXIII	10/1	1.0	6.6	116 (248)	0.090 (0.089)
XXIV	20/1	0.3	5.1	98 (247)	0.086 (0.089)

[a] Actual vs (theoretical) values.

TABLE 5

Plating Results and Concentrate Appearance

Run	$KCl/PdCl_2$ ratio	Test panel plating (%)	Catalyst appearance
		K_2PdCl_4 addition	
XV	2/1	100	Hard solid
XVI	3/1	100	Hard paste
XVII	4/1	100	Softer paste
XVIII	10/1	100	More crystals than liquid
XIX	20/1	100	Equal amounts crystals and liquid
		$PdCl_2$ addition	
XX	1/1	1	Hard solid
XXI	2/1	60	Hard paste
XXII	4/1	30	Softer paste
XXIII	10/1	40	More crystals than liquid
XXIV	10/1	50	Equal amounts crystals and liquid

containers in a liquid state at room temperature for several days. They then rapidly nucleate and release large amounts of heat during crystallization.

The physical form is easily explained by the formation of salts such as $KSnCl_3 \cdot H_2O$. $SnCl_2 \cdot 2H_2O$ is so soluble that the excess water released on formation of the potassium compound keeps much of it in solution. The potassium salt has been isolated and verified by analysis.

Variation of Added Halide Salt

A final series of catalysts was run using a number of halide salts added directly to the melt. As was shown for KCl, this procedure is not as good as the use of the double palladium salt, but will serve to rank the compounds. The following salts were ineffective: $AlCl_3$, $PbCl_2$, $ZnCl_2$, and $FeCl_3$. Test runs were made by dissolving 1 g $PdCl_2$ (0.0056 *M*) in a 95°C melt of 37.9 g (0.168 *M*) $SnCl_2 \cdot 2H_2O$ containing 2.63 g NaCl (XXV), 5.35 g KBr (XXVI), 3.35 g KCl (XXVII), 4.56 g $MgCl_2 \cdot 6H_2O$ (XXVIII), 5.35 g $NiCl_2 \cdot 6H_2O$ (XXIX), 5.5 g $LaCl_3 \cdot 7H_2O$ (XXX), or 4.0 g $CrCl_3 \cdot 6H_2O$ (XXXI). The reaction time was 15 min. The amounts of added salts correspond to 8 moles of added halide (not halide salt) per mole of $PdCl_2$. Table 6 shows the data.

All of the salts listed gave active catalysts, though the activity of $NiCl_2 \cdot 6H_2O$ (XXIX) and $CrCl_3 \cdot 6H_2O$ (XXXI) was low. For this reason, the working bath concentration for these two preparations was three times greater than for the other runs. Performance was still marginal in initiation of electroless plating. The KBr run was one of the best of any tested under unoptimized conditions. Both palladium and tin absorptions were several times greater than in any other run, and catalytic activity in the electroless nickel bath was excellent.

The physical form of the catalyst was dependent on the amount of water added in the form of the chloride salt, and the specific salt formed with $SnCl_2$ on cooling. Thus KCl produces $KSnCl_3 \cdot H_2O$ and sets free one H_2O from $SnCl_2 \cdot 2H_2O$. NaCl reacts to give $NaSnCl_3$, with two freed water molecules. The former would give a less liquid final catalyst concentrate at comparable levels of added halide. The results are summarized in Table 7.

An easier way to make a uniformly solid catalyst is to control the total water content by adding mixtures of $SnCl_2 \cdot 2H_2O$ and anhydrous $SnCl_2$. This type of melt reacts in a fashion similar to that of the pure $SnCl_2 \cdot 2H_2O$ melt. However, the anhydrous $SnCl_2$ can be added in any amount to control the final physical form of the catalyst concentrate.

Oxidative Stability

Commercial plating catalysts must be optimized for a large number of factors. These include physical form and stability of the concentrate, interaction with (absorbability on) specific polymers, activity of the absorbed catalyst, and oxidation resistance of the catalyst working bath.

The baths are fairly stable in the absence of air, but slowly oxidize during use. The activity and appearance of the working baths do not greatly change as long as at least 5–10% of the original stannous content is present. As the last amounts are oxidized, the color changes from an opaque

TABLE 6

Effect of Halide Salt Variation

Run	Halide added	Absorption (10^{-6} g/cm^2)		Working bath concentrations[a]	
		$PdCl_2$	$SnCl_4$	$PdCl_2$ (mg/liter)	Sn (*M*/liter)
XXV	NaCl	1.6	4.4	134 (250)	0.042 (0.042)
XXVI	KBr	4.8	13.1	231 (249)	0.039 (0.042)
XXVII	KCl	1.5	5.8	166 (248)	0.045 (0.042)
XXVIII	$MgCl_2 \cdot 6H_2O$	1.1	4.4	143 (249)	0.042 (0.042)
XXIX	$NiCl_2 \cdot 6H_2O$	0.4	4.4	266 (723)	0.134 (0.122)
XXX	$LaCl_3 \cdot 7H_2O$	0.7	2.9	140 (252)	0.042 (0.042)
XXXI	$CrCl_3 \cdot 6H_2O$	0.8	5.1	310 (729)	0.129 (0.123)

[a] Actual vs (theoretical) values.

red-brown to a transparent yellow. The decomposed catalysts give the uv–visible spectrum of $PdCl_2$ and $SnCl_4$; precipitates containing palladium and/or Pd/Sn can also form.

Several methods are available to retard the oxidation, including exclusion of air, addition of metallic tin, or use of polyhydroxy oxidation inhibitors such as resorcinol (*4*, *21*, *50*). During the course of this work, it was found that the hydrous melt synthesis method unexpectedly gave markedly lower stannous oxidation rates. The rates were found to be related to heating temperatures and reaction times, along with other factors.

Table 8 shows a comparison of two commercial liquid catalysts with a hydrous melt catalyst prepared in a manner similar to XVIII. The stannous contents of each solution were measured before testing and adjusted to ±0.25 g/liter. Initial concentrations were approximately 0.096 *M*/liter (13 g/liter). The catalyst prepared using a hydrous melt oxidized at half the rate of the best commercial liquid catalyst.

A major influence on the oxidation resistance is the length of heating of the hydrous melt. Extended heating times give more slowly oxidizing products. One experiment gave a life of 18.5 hr/g $SnCl_2$. This might imply that polymeric stannous species are formed in the melt, which then oxidize more slowly when dissolved in hydrochloric acid. Further work is being done on this aspect of the synthesis.

SUMMARY

This work describes an interesting new way to prepare tin–palladium electroless

TABLE 7

Plating Results and Concentrate Appearance

Run	Salt added	Test panel plating (%)	Catalyst appearance
XXV	NaCl	100	More liquid than crystal
XXVI	KBr	100	Soft paste
XXVII	KCl	100	Hard paste
XXVIII	$MgCl_2 \cdot 6H_2O$	80	Equal amounts liquid and solid
XXIX	$NiCl_2 \cdot 6H_2O$	25	Equal amounts liquid and solid
XXX	$LaCl_3 \cdot 7H_2O$	80	Mostly liquid
XXXI	$CrCl_3 \cdot 6H_2O$	60	Mostly liquid

TABLE 8

Accelerated Oxidation Rate Testing

Catalyst	Catalyst life (hr)	Catalyst life (hr/g $SnCl_2$)
Liquid A[a]	20.25	6.20
Liquid B[a]	14.0	4.28
Hydrous melt	38.0	11.64

[a] Commercial liquid tin–palladium catalysts; A is a "colloid"; B is a "complex."

plating catalysts using hydrated melts. These catalysts have activities which can be as good as or better than those of catalysts prepared using aqueous acid procedures. A wide range of compositions and water contents can be used to give widely varying results. The physical form of the final product can be varied easily. This process may also be useful for studying the reactions of other Group VIII metals with stannous chloride.

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