Generative and Stabilizing Processes in Tin-Palladium Sols and Palladium Sol Sensitizers

R. L. Cohen and K. W. West

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

ABSTRACT

An extensive study of sol systems produced by the reduction of solvated Pd by Sn^{2+} is presented. We show that the reaction is initiated by the formation of a polynuclear Sn-Pd complex, which is autoreductive, yielding sol particles of a Sn-Pd alloy core with a stabilizing layer of Sn^{2+} ions. The role of the Sn^{2+} stabilizing layer in controlling particle size is discussed in detail. We apply the knowledge of these systems to understand similar processes occurring in commercial Pd sol systems used for sensitizing insulating surfaces for electroless plating. The chemistry of the sensitizing layer generated by these systems has also been studied. The sol sedimentation rate has been studied by centrifugation. Most of the investigation has been carried out via Mössbauer spectroscopy; precise isomer shift parameters for a number of Sn-Pd compounds are reported.

Electroless plating to metalize insulating substrates generally requires a preliminary treatment of the surface to make it catalytic (also called "active" or "sensitive") to initiate the deposition of metal from the electroless bath. An overview of the approaches used has been given by Goldie (1). For many years, the most common preparation process was a two-stage treatment, in which the surface was immersed first in a dilute stannous chloride solution, and then in a dilute palladium chloride solution. We have recently reported (2, 3) a detailed description of the chemical processes and reactions of the two-step process, based on the results of Mössbauer spectroscopy measurements on the tin compounds and complexes formed.

Key words: sensitization, colloids, tin chemistry, palladium chemistry, Mössbauer spectroscopy.

More recently, a number of proprietary systems achieving "sensitization" with only a single-stage treatment have become available. The advantage of the single-stage system goes beyond the elimination of one bath; it makes possible the elimination of intermediate washes, re-racking, and drag-in problems. A number of proprietary[1] single-stage sensitizers are available; all involve tin and palladium. Two of the systems (4, 5) are stated to be Pd sols stabilized by a "protective colloid." These systems are somewhat similar involving mixtures of Sn^{2+} and Pd^{2+} ions, HCl, and water; the concentrations and order of addition are varied. Tetravalent tin may be also added to

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[1] The proprietary single-stage sensitizers referred to are the Shipley Corporation 6F sensitizer (4), the MacDermid Corporation Metex PTH 9070 sensitizer (5), and the Dynachem Corporation Activator 101 and 120.

improve wetting of hydrophobic substrates. The evidence is that the palladium colloid coats the substrate in the treatment process, and subsequently is the active agent that nucleates deposition from the electroless bath.

This paper reports the results of measurements by Sn^{119} Mössbauer spectroscopy on the tin components used in the palladium colloid, and an investigation of the colloid formation and stabilization. Special emphasis is placed on the way the colloid-forming reactions determine the properties of the resultant sol. We also discuss the results of Mössbauer measurements on the sensitizing layers themselves. An additional experiment on centrifugation of the commercial sensitizer systems has also been performed to give some idea of the particle size distribution.

The patents describing preparation of two of the one-component systems discuss procedures which are similar in outline, but different in detail. Rather than following analytically each of these "recipes," we have performed a series of experiments which establish the basic chemical stages characterizing the over-all process. The preparation procedures of the individual patents can then be viewed in the light of the findings we present.

This paper deals with a number of very different aspects of the Sn-Pd sol system, and we have modified the normal order of presentation to maintain clarity. We begin with a brief description of the experimental techniques used for the Mössbauer spectroscopy measurements, and a discussion of the interpretation of the spectra obtained. The next section of the paper discusses the formation and identification of a tin-palladium complex which is critical to the colloid formation process. This is followed by a description of the colloid formation as the complex decomposes, and characterization of the components of the colloid from its Mössbauer spectra. In the last third of the paper, the knowledge of the tin-palladium colloid system is used to understand the "recipes" described in the patents for the commercial sol systems and the chemistry of the sensitizing layer deposited on the dielectric. In the last part of the paper, the relation between solution chemistry and particle size in the colloid is also discussed.

Mössbauer Spectroscopy

Experimental techniques and interpretation of spectra.—The experimental techniques used are essentially those discussed in Ref. (2) and (3), and are standard for tin Mössbauer spectroscopy. The source consisted of about 8 mCi of Sn^{119m} in the form of $BaSnO_3$, and was kept at liquid nitrogen temperature.[2] Absorbers were made by freezing the solutions in liquid nitrogen in plastic capsules about 8 mm deep.[3] These capsules were stored and the measurements were made at liquid nitrogen temperatures. A standard transmission-geometry Mössbauer spectrometer was used, with the source being moved by an electromagnetic drive system (8). Data were taken using time-mode up-down multiscaling in a multichannel analyzer, and the figures shown here are traced from the analyzer plotter output. Least squares analysis of the data, and "spectrum stripping" to reveal minor spectral components more clearly, were done as described in the text and figure captions.

Both the systematics and details of the interpretation of Sn^{119} Mössbauer spectra have been extensively discussed in various reviews (9, 10). Only a few different types of tin-containing compounds are involved in this study, and it is possible to identify them, and thus to use the spectra for analysis, by comparison with "standards" of known composition. For convenience, the isomer shifts and quadrupole splittings determined have been listed in Table I. The major features which repeatedly appear, and will be important for the interpretation of the data, are:[4]

Table I. Isomer shift and quadrupole splitting (in mm/sec) for Sn^{119} in materials studied here

	Material	Isomer shift[a]	Quadrupole splitting[e]
Alloys[b]	$Sn_{0.05}Pd_{0.95}$	1.55	—
	$Sn_{0.09}Pd_{0.91}$	1.53	—
	$Sn_{0.14}Pd_{0.86}$	1.57	—
Intermetallics[f]	Pd_3Sn	1.87	—
	Pd_2Sn	1.62	0.73
	PdSn	2.01	0.62
	$SnO_2 \cdot nH_2O$	0.00	0.55
Frozen solutions	Sn^{2+} in 30% HCl[c]	3.56	1.13
	Sn^{4+} in 30% HCl[c]	0.32	0.43
	Pd(II) · 3Sn(II) complex in 30% HCl	1.42	1.98 ± 0.02
	"PdSn" complex[d]	1.37	2.21 ± 0.05

[a] Quoted with respect to $BaSnO_3$ at 78°K; all absorbers were at 78°K during the measurement. Error ±0.04 mm/sec.

[b] Isomer shift differences among these alloys are significant, but may simply reflect clustering phenomena in these disordered alloys.

[c] These materials contain a number of different complexes; the parameters quoted simply describe a "best fit" of a doublet of the data, and do not characterize any particular complex.

[d] From Ref. (15), extracted as the tetramethylammonium salt. (Isomer shift value converted assuming that the isomer shift of α-tin is 2.00 mm/sec with respect to $BaSnO_3$.)

[e] Obtained by least squares fitting doublets to unresolved broad lines. Estimated accuracy ±0.2 mm/sec, except for Pd(II) · 3Sn(II).

[f] These data are in fair agreement with those of Ref. (11) insofar as it is possible to compare them.

1. Sn^{2+} ions, OH^- or Cl^- complexed, give a doublet in the absorption spectrum, centered near +3.6 mm/sec (Fig. 1A).

2. Sn^{4+} ions, bare or complexed, give a broad absorption line (Fig. 1B), near zero velocity.

3. Sn-Pd alloys (11)[5] give a singlet or barely resolved doublet, at about 1.5-2 mm/sec (depending on the Sn-Pd ratio, see Fig. 1C and 1D and Table I).

In all of the results, of course, the spectra are those of the Sn^{119} component of the compound; the chemical state of the palladium can only be inferred from its connection with the tin.

Results and Discussion

Complex formation.—The first part of the experimental work reported here was successful in elucidating the details of the formation of the Pd colloid, and the intermediate reactions. These results are very closely connected with the formation of a Sn-Pd complex. The literature contains a number of reports of tin-palladium complexes, discussing the theoretical and structural chemistry (12, 15),[6] of this system as well as the applications (12, 14, 16). Briefly summarizing, the addition of Sn^{2+} to HCl solutions containing small quantities of Pd^{2+} ions results in the formation of a series of highly colored complexes, which are unstable (14). These are variously reported as being red, brown, yellow-green, and bluish green, depending on the concentration of various species and the solution age. So far as we know, no crystal structure determination on a solid derivative of the Pd-Sn complexes has been performed, and the structures shown in the research articles are either conjectural or based on analogy with similar transition metal complexes.

We investigated the complex by combining two solutions:

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[2] The isomer shift of this source with respect to a high-purity $BaSnO_3$ absorber at 78°K was less than 0.01 mm/sec. We are greatly indebted to Dr. P. K. Gallagher of this laboratory for supplying this material.

[3] We have recently discussed the necessity of having glass-forming systems if "frozen solution" Mössbauer spectroscopy experiments are used to characterize the liquid phase (6). In the systems studied here, the presence of 30% (or more) HCl in the solutions served as the glass-forming agent (7). We were able to verify the effectiveness of the glass-forming process both by visual observation of the solutions during freezing and auxiliary experiments with added glycerol as a glass-forming agent.

[4] The major complexing reactions for Sn^{2+} and Sn^{4+} in HCl solutions have been summarized in Ref. (3).

[5] We have also made Sn-Pd alloys and several Pd-Sn intermetallics in our laboratory, and the spectra of these materials are shown in Fig. 1. Values shown in Table I come from measurements on materials made by us.

[6] Baranovskii *et al.* (15) give quadrupole splitting and isomer shift values for a complex which they identify as $(PdCl_2(SnCl_3)_2)^{2-}$, extracted from HCl with hexyl alcohol and as tetramethylammonium salts.

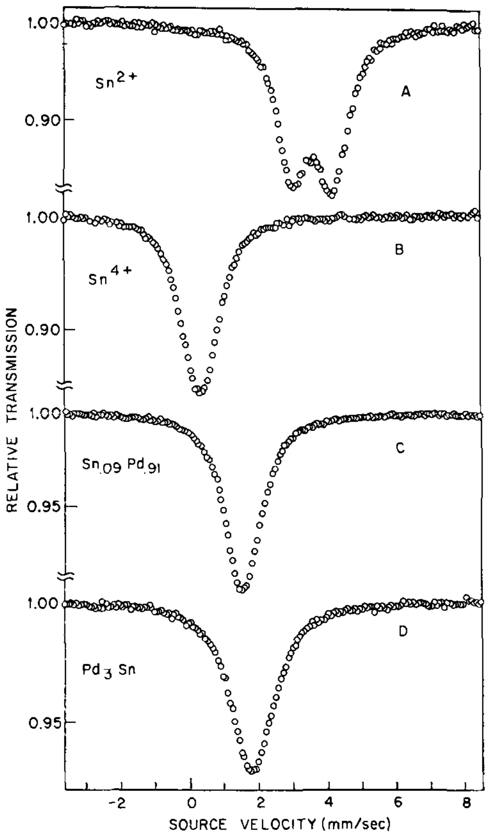

Fig. 1. Mössbauer spectra of pure phases of some tin species encountered in the solutions studied; for comparison with data in other figures. A and B, spectra of Sn^{2+} and Sn^{4+}, respectively, complexed ions dissolved in 4M HCl. C and D, spectra of $Sn_{0.09}Pd_{0.91}$ alloy and Pd_3Sn.

Pd soln.	100 mg	$PdCl_2$ (Fisher)
(11 mM in Pd^{2+})	10 ml	37% HCl (reagent grade)
	20 ml	H_2O (distilled)
Sn soln.	Amount given in text	$SnCl_2$ (purified to remove Sn^{4+})
	1 ml	37% HCl
	2 ml	H_2O (distilled)

The solutions were made slightly above room temperature and cooled to ~0°C (see below); they were maintained under nitrogen gas at all times to prevent oxidation. The Pd solution had a pale orange color; the Sn solution was essentially colorless. These two solutions were combined with rapid stirring, and an intense reddish-brown color formed instantly.

Figure 2A shows the Mössbauer spectrum of a sample of the mixture taken and frozen within 10 sec after combining the Sn and Pd solutions. The most obvious feature of that spectrum is that the doublet characteristic of SnCl complexes (Fig. 1A) is not visible; it has been replaced by another doublet, which our results show arises from the red-brown Sn-Pd complex in HCl. We have explored a range of Sn-Pd ratios and find that for $Sn/Pd < 3$, all of the tin is immediately complexed to produce the spectrum of Fig. 2A, while for $Sn/Pd > 3$, additional components which can be identified as arising from SnCl complexes (as in Fig. 1A), appear. Thus each Pd ion complexes three Sn ions, and we conclude that the stoichiometry of the Sn-Pd complex is $Pd(II) \cdot 3Sn(II)$. We abbreviate the dissolved complex as $(Pd\text{-}Sn)_c$ below. This is consistent with the results of Batley and Bailar (12) who suggest $(PdCl)(SnCl_3)_3{}^{2-}$ for the structure of the complex precipitated (from an HCl-methanol solution) using tetraphenylarsonium chloride.

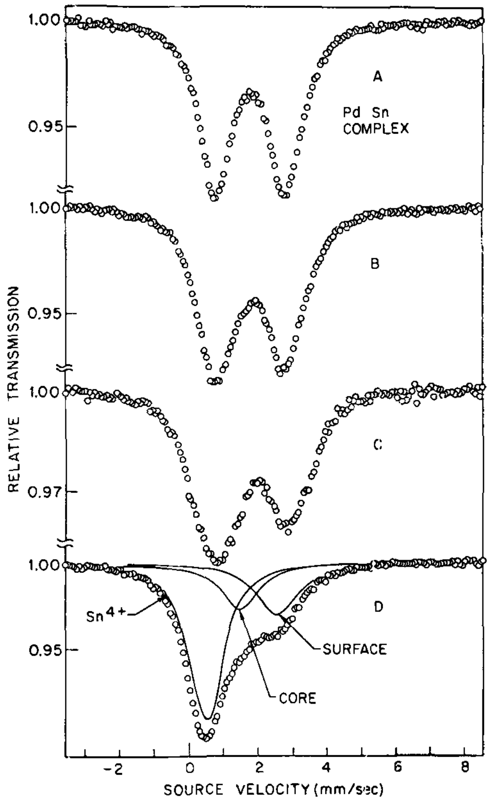

Fig. 2. Spectra of Sn-Pd complex solutions (Sn/Pd ratio 2:1) at (A) 0.2 min, (B) 6 min, (C) 30 min, (D) 120 min after mixing. The doublet in (A) is due to the Sn-Pd complex. This decomposes with time, producing complexed Sn^{4+} due to the redox reaction, Sn-Pd alloy, a small amount of dissolved Sn^{2+}, and a line which we attribute to a protective Sn^{2+} layer surrounding the Pd-Sn sol particles.

Colloid generation.—The Pd colloid begins to form immediately after the complex is made, and we found it necessary to cool the Pd solution (as mentioned above) to make the reaction proceed slowly enough to be monitored conveniently. As shown in the Mössbauer spectra (Fig. 2), the spectrum of the complex is gradually replaced by three new components. These are identifiable (with the help of subsidiary experiments) as (*a*) dissolved complexed Sn^{4+}, (*b*) the tin protective layer, and (*c*) Sn in Pd-Sn alloy. While it is difficult to resolve the line arising from the alloy from that of the dissolved Sn^{4+}, the colloid can be separated (see below) either by coagulation or centrifugation. It is the spectra of separated materials that allow the identification of the particulate phase as Sn-Pd alloy.

Neglecting for the moment the Sn component in the alloy, this decomposition to produce the Pd colloid would be expected to result from

$$(Pd\text{-}Sn)_c \rightarrow Pd_{metal} + Sn^{4+} + 2Sn^{2+} \qquad [1]$$

During this decomposition process, the red-brown color of the solution changes to a muddy grayish-brown, and then eventually to gray, corresponding to the destruction of the complex. This autoreduction of the Sn-Pd complex is probably the cause for the disappearance of color with time in the use of the Sn-Pd complex test (14) for trace amounts of Pd.

It is instructive to consider four different ratios of Sn/Pd describing the process. For $Sn/Pd = 1$, the divalent tin is consumed in reducing the palladium, and the spectrum shows only lines attributable to dissolved Sn^{4+} and Sn-Pd alloy. There is no line attributable to stabilizing Sn^{2+} visible in the spectrum, and the sol is in fact unstable and coagulates rapidly.

For $Sn/Pd = 2$, not all of the Pd is immediately complexed, since the stoichiometry of the complex is Pd:3Sn. As the redox reaction [1] occurs, some Sn^{2+} is returned to the solution, where it is immediately complexed by the remaining Pd. Some Sn^{2+}, however, remains attached to the Pd metal. This Pd metal can become a nucleus for growth by attaching other Pd metal-tin clusters, and can grow until the Pd core is completely surrounded by Sn^{2+} ions. At this point the growth ceases. This model provides (*i*) a mechanism for particle growth, and (*ii*) a mechanism for terminating the growth and preventing coagulation. Note that if, after the complex-reduction process is complete, the colloidal particles are not completely surrounded by Sn^{2+} ions, they will agglomerate. This process decreases the surface: volume ratio until the amount of Sn^{2+} present is enough to coat the remaining particles.

In the Centrifugation section at the end of the paper we discuss the effects of the amount of available Sn^{2+} in controlling the colloid particle size. The spectra of Fig. 2 show clearly that the complex decomposes completely, leaving (dissolved) Sn^{4+}, a tin-palladium alloy phase, and a third component, which we identify below as the Sn^{2+} stabilizing layer. For the ratio $Sn/Pd = 2$, there is just enough divalent tin to reduce the Pd and stabilize the colloid; no dissolved Sn^{2+} is observed after the reaction is complete.

For $Sn/Pd = 3$, all the tin and palladium are immediately complexed; the spectra again show the Sn-Pd alloy phase, Sn^{4+}, and the tin stabilizing layer, but show additional lines, arising from dissolved Sn^{2+}, after the complex has decomposed.

For $Sn/Pd > 3$, all the Pd is initially complexed, and dissolved Sn^{2+} is observed in the spectrum at all times. Figure 3A shows an example of such a solution, in which a substantial amount of dissolved Sn^{2+} is present after the decomposition is complete.

Visual observations of the color change of the solution show that the decomposition of the complex (as monitored by the disappearance of the red-brown color) is very much slower in tin-rich solutions than in the mixture used for Fig. 2. This has been confirmed by Mössbauer spectroscopy of the frozen solutions.

This probably results from two phenomena. First, the presence of excess dissolved Sn^{2+} forces reaction [1] to the left, increasing the amount of complex at equilibrium. (This residual complex may provide the brownish color in the commercial sol sensitizers.) Second, if large amounts of Sn^{2+} are dissolved, they will immediately coat and passivate fresh sol particles which could otherwise act as nucleation centers for the accretion of additional Pd metal and as catalytic centers for the Pd reduction reaction. At a constant Sn/Pd ratio, the rate of decomposition of the complex was not noticeably affected by increasing the starting concentration by a factor of four over that described above.

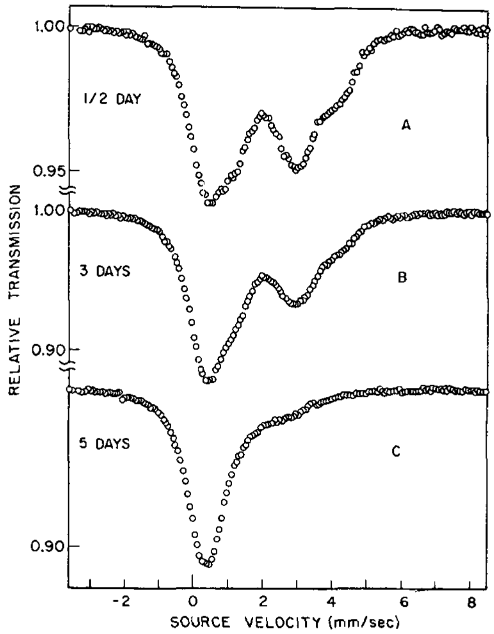

Fig. 3. Spectra showing air oxidation of Sn-Pd sol, made as described in text, but with Sn-Pd ratio of 6:1. The bath was aged at room temperature in an open beaker; (A) ½ day, (B) 3 days, (C) 5 days after Sn-Pd mixing. Initially, most of the Sn^{2+} is complexed in the HCl solution (compare Fig. 1A), and it tends to hide the line originating from the protective Sn^{2+}. As the dissolved Sn^{2+} ions are progressively oxidized, the Sn^{4+} line grows and begins to hide the Sn-Pd alloy line although the latter does remain constant in intensity. Note the line at ~3 mm/sec, due to the Sn protective layer. Coagulation occurred a few hours after sample (C) was taken.

We have not been able to determine in detail the chemical mechanism that incorporates the tin in the colloid, but a number of redox reactions involving $(Pd\text{-}Sn)_c \rightarrow (Sn\text{-}Pd)_{alloy} + 2Sn^{4+}$ would be possible.

Composition of solid phase.—One preparation patent (5) states that the Pd colloid is stabilized by a "protective colloid" of Sn^{2+} ions. This picture is supported by the fact that if the solution containing the colloid is allowed to oxidize by contact with air, the particles suddenly coagulate and precipitate just as a Mössbauer spectrum of the frozen bath shows that all the dissolved Sn^{2+} ions in the bath have been oxidized to Sn^{4+}. This coagulation is characteristic of all of the commercial systems. Figure 3 shows spectra taken during this air-oxidation process; lines from the dissolved (Cl^- complexed) Sn^{2+} ions are seen to decrease while the Sn^{4+} line grows in intensity. Just before precipitation, (Fig. 3C), no dissolved Sn^{2+} is visible, but another Sn^{2+} line is visible. We attribute this line to the protective Sn^{2+} layer on the sol particles. This interpretation is supported by the fact that we observe this line only in the colloidal suspensions, and that it disappears just as the colloid coagulates. This, plus the fact that no ionic Sn compound composed of the available ions has a line in the position observed, provides strong evidence that the tin ions involved are at the colloid surface. A likely configuration for such a layer could be for $(SnCl_3)^-$ complexes (which were originally components of the Sn-Pd complex) to be bonded to the Pd-Sn alloy core via Sn-Pd bonds, with the Cl^- ions on the outside.

After coagulation, the supernatant contains only Sn^{4+} ions, while the coagulated solid phase consists of Sn-Pd alloy, plus a small quantity of Sn^{4+} ions. Spectra of these materials are shown in Fig. 4.

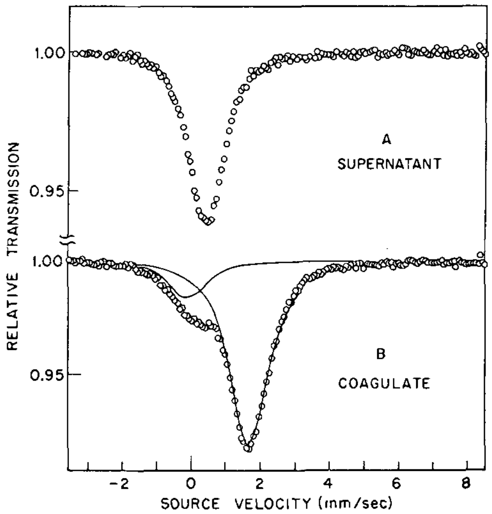

Fig. 4. Spectra of (A) supernatant and (B) coagulated precipitate (washed with H_2O) immediately after coagulation of the colloid following air oxidation of Pd sol used in Fig. 2. Note that no Sn^{2+} ions remain in solution, and that the Sn^{2+} line which we have ascribed to the stabilizing tin layer is no longer present. The Sn^{4+} line visible in the precipitate is characteristic of the $SnO_2 \cdot nH_2O$ family of compounds and results primarily from precipitation during the H_2O wash. Coagulates washed with HCl have relatively little Sn^{4+}.

It is possible to observe the particulate phase much more clearly in colloids in which it has been concentrated by centrifugation. Figure 5A shows such a spectrum, and its resolution (17)[7] into Pd-Sn alloy and the stabilizing Sn^{2+} layer. Instead of washing the centrifuged material to remove traces of electrolyte containing dissolved Sn^{2+} and Sn^{4+} ions, we have taken spectra of the supernatant and subtracted a small fraction of the supernatant spectrum from the spectrum of the sedimented material. In this way, we could eliminate the lines due to dissolved tin ions without coagulating or otherwise changing the colloid in the process of making the absorber. Centrifugation did not coagulate the colloidal particles; they would redisperse spontaneously after standing for a few days. All of the measurements on the commercial sensitizers were done using the undiluted "stock solution" concentration, as supplied by the manufacturers.

Spectra such as those in Fig. 5A allow accurate determinations of line positions of the various components, and least squares fitting has shown small variations in isomer shift and line width for both the core and stabilizing layer components. Isomer shift values for the "Sn-Pd alloy" cores have been found to be up to 0.15 mm/sec less than values for the metallurgically prepared alloys shown at the top of Table I. This is very likely due to the lattice contraction occurring in very small particles.

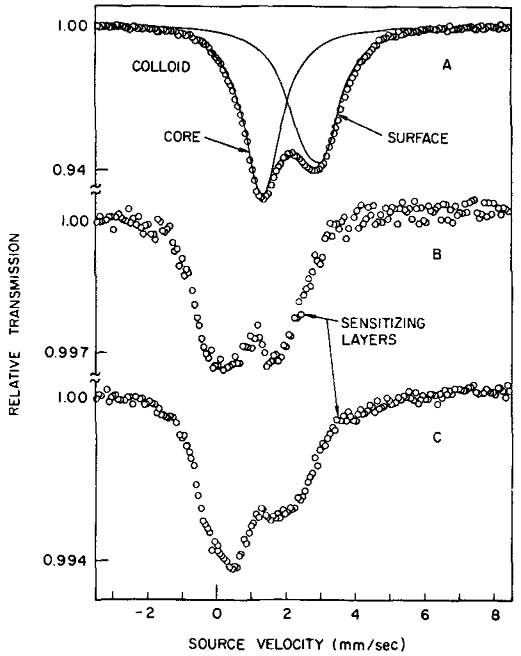

Fig. 5. Spectrum of sol particles (A), concentrated by centrifuging. This shows clearly the two lines which we attribute to the Pd-Sn alloy cores of the sol particles, and the broader line we ascribe to the stabilizing layer. This sample, made with a Sn/Pd ratio of 3, had finer particle size than the solutions shown in Fig. 6, and would be expected to have a relatively large amount of tin in the stabilizing layer, (*i.e.*, the smaller sol particles should have a large surface to volume ratio). Spectra of sensitizing layers (B and C) deposited on Kapton foil using MacDermid Metex PTH 9070 in accordance with the standard MacDermid dilution instructions. The (B) sample (688 layers) was rinsed with 0.5M HBF_4 as an "accelerator" (5) and then with water after sensitization; (C) (456 layers) was rinsed in water. The additional spectral intensity in (C) just to the right of the Pd-Sn alloy peak could very well arise from the mixed-valence (Sn^{2+} and Sn^{4+}) colloid shown in Fig. 6A of Ref. (3) (that material was produced by increasing the pH of a solution of Sn^{2+} and Sn^{4+} in HCl), or could be (3) $SnO \cdot 2H_2O$. Thus, the role of the accelerator is to remove the divalent tin so that it is not precipitated when the pH is raised during the wash step (see footnote 4). We were able to verify that the fluoborate ion is a complex former with Sn^{2+} in the concentrations used here.

Mössbauer measurements in very fine supported gold sols have already demonstrated the existence of this effect (18) and have shown that the observed isomer shift is the same as would be expected if the decrease of the lattice constant were produced by hydrostatic pressure (19). In the case of the Sn-Pd alloys, experiments on the variation of the isomer shift with (pressure-induced) lattice contraction have already been performed (20). The decrease in the lattice constant in Pd-Sn alloy under pressure decreases (20) the electronic density at the tin nucleus; this would produce a smaller isomer shift under lattice contraction, which is what we observe. Using the results of Ref. (20), we can estimate that the change in isomer shift we observe in the smallest sol particles corresponds to a contraction that would be produced by pressures of 100-200 kbar. Such high pressures are in line with previous observations on gold sol particles of comparable size (21).

X-ray measurements were made to determine the lattice constant and structure of the coagulated sol particles. These showed a pattern with only very broad lines, due to compositional inhomogeneities, small particle size, or strain. The lattice constant was appropriate for an alloy containing about 16% Sn in Pd, near the solid solubility limit.

Small variations in the isomer shift and line width of the Sn^{2+} stabilizing layer would be expected to arise from changes in the site (on the Pd-Sn core) to which the stabilizing tin was bound.

We also observed a small increase in isomer shift of the sol particle phase upon coagulation, and some precipitates actually had slightly larger isomer shifts than the Sn-Pd alloy. This probably arose from the incorporation of some of the Sn^{2+} stabilizing ions into the outer layers of the sol particle; as can be seen from Table I, all of the intermetallics containing more than 15 atomic per cent tin had larger isomer shifts than the Sn-Pd alloy.

Extension of Results to Commercial Sensitizer Systems

The results reported above are based on studies of solutions which differ in various ways from those sold commercially, and we have attempted to verify that the mechanisms that we describe are valid for those solutions. We have done this both by ultracentrifuging (which concentrates the particulate phase without coagulation) and by coagulating samples of the proprietary baths to concentrate the solid phase, and taking spectra of the precipitates. For the 6F and 9070 sensitizers, the colloid spectra were very similar to those of Fig. 5A, with minor differences attributable to different proportions between the Pd-Sn alloy and stabilizing Sn^{2+} components, and some uncertainty arising from the background subtractions as described above. The supernatant after centrifuging always appeared to be a simple mixture of dissolved Sn^{2+} and Sn^{4+} ions, as in Fig. 1A and 1B. This confirms the generalization of our results to the commercial systems described in Ref. (4) and (5).

We have also studied the reactions occurring in Sn-Pd solutions in concentrated (*i.e.*, 37%) HCl, and have found that the Mössbauer spectrum of the Sn-Pd complex produced is identical to that shown in Fig. 2A; this is good evidence that the complexes are identical. Although complex formation in the concentrated HCl is essentially instantaneous, the autoreduction reaction [1] is slower, and is still further slowed if a large excess of Sn^{2+} is present. Judging from the color of the solution, however, most of the complex has decomposed within 24 hr at room temperature. The sol produced from a tin-rich solution also contains a higher concentration of tin in the alloy, with the isomer shift of the coagulated particles approximately that of Pd_3Sn. No other attempt was made to stabilize the complex.

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[7] We have previously written a brief report (17) of the analysis of the particulate phase of these sols.

Sensitization Mechanism

The information above is consistent with the over-all picture [discussed, *e.g.*, in Ref. (4) and (5)] that sensitization occurs via the adsorption of Pd particles on the surface, and that the Pd alloy is the active agent in catalyzing deposition from the electroless solution. The detailed information above on the colloid composition and stabilization may lead to some additional understanding of the adhesion process, and we have supplemented studies of the baths with measurements of the sensitizing layer on a plastic surface.

Figure 5 shows Mössbauer spectra of many layers of Kapton^R plastic film, sensitized with a commercial bath, given various rinse treatments, and dried in nitrogen. The surfaces were checked with a standard copper electroless solution to verify that sensitization had indeed occurred. The use of the "accelerator" wash dramatically increased the catalytic activity of the surface. The spectra are somewhat different from those of the sol particles; a strong line characteristic of stannic hydroxide appears, and the line (attributed in Fig. 5A to the stabilizing Sn^{2+}) is no longer present. Lines due to dissolved Sn ions are, of course, absent.

The differences can be readily explained on the basis of what is known about the chemistry of these colloids. When the substrate is immersed in the sensitizing bath, in addition to the adsorption of the sol particles, there will be some oxidation of the Sn^{2+} by oxygen adsorbed on the substrate and by dissolved oxygen in the solution used for surface pretreatment. (Note that the amount of Sn^{2+} deposited corresponds to only ≈ 1 monolayer, assuming uniform coverage, so that only very small amounts of dissolved oxygen suffice to produce this oxidation.) The chemical reaction at the interface could possibly promote stronger adhesion of the colloid particles since ionic, rather than van der Waals bonding, would then be operative.

Centrifugation Experiments

As a corollary to the Mössbauer experiments, samples of the concentrated commercial sensitizer formulations were centrifuged to determine qualitatively their particle size and size distributions. The results of those experiments are shown in Fig. 6, as photographs of the vials after centrifugation. The variation of optical density of the samples gives some indication of the particle size distribution. Note that for all the commercial formulations shown, the top layer of the vial is essentially colorless, indicating that the smallest particle size with substantial population is $\sim >10$Å diameter.[8] However, the well-known Stokes-law breakdown is significant in this size range, and, more important, there is probably a large shell of Cl^- ions complexing the tin protective layer, and this would greatly decrease the effective density of the particle. Thus, the lower end of the colloidal particle size distribution is probably about 20Å in diameter.

Earlier in the paper we discussed the limitation of particle growth by the stabilizing layer of Sn^{2+}, and control of particle size by this mechanism. In the model presented, particles would grow and agglomerate until they were covered by a layer of Sn^{2+} ions [probably as $(SnCl_3)^-$ complexes], after which growth would stop. We have performed a critical test of this model, as follows: tin-palladium sols were made (starting with 100 mg $PdCl_2$ in 10 ml + 20 ml H_2O) using Sn/Pd ratios of 1.2, 1.5, 2 and 2.5 and 3. The complex was allowed to decompose at room temperature under nitrogen gas, to avoid oxidation. After the decomposition was complete (12 hr), some additional Sn^{2+} (Sn/Pd = 1) was added to decrease the sensitivity of the solutions to oxidation, and the mixtures were centrifuged. The results, in Fig. 7, show graphically that the smaller the amount of excess Sn^{2+} present when the sol was forming, the larger the particles grew before they were stabilized. This is exactly what the model would have predicted.

Fig. 6. Photographs of vials containing commercial sensitizers after centrifugation at 110,000G at 15°C. Centrifuging times are (from top) 4, 21, and 29 hr; samples are (from left) MacDermid 9070 and Shipley 6F.

Fig. 7. Photographs of centrifuged Sn-Pd sols, made as described in text. With Sn/Pd = 1.5 and 1.8, coagulation occurred spontaneously within a few hours. The photograph shows sols with Sn/Pd = 2, left, and Sn/Pd = 2.5, right. An additional experiment with Sn/Pd = 3 (not shown) produced still finer particles. The decrease in particle size with increasing Sn/Pd ratio supports the picture of sol formation and particle stabilization given in the text. Centrifugation conditions were 15 hr at 110,000G. Note that the sedimentation rate for the left vial is essentially the same as that of the MacDermid colloid (Fig. 6), which is also generated with Sn/Pd = 2.

This approach can also be used to understand the differences in particle size distribution between the Shipley 6F and MacDermid 9070 sensitizer solutions. The Shipley process (4) generates the sol by mixing the Pd solution into a solution containing a large excess of Sn^{2+}. This should provide the finest possible

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[8] We assume that Sn-Pd alloy has a density of 10 g/cc and that the viscosity of the electrolyte (at ~15°C) is the same as that of water at 20°C. Uncertainties arising from the presence of the shell of solvating ions are far larger than these approximations. Electron micrographs of the sol particles in the commercial systems show spherical particles, typically ~100Å in diameter (22).

particle size, as the sol particles are quickly covered by Sn^{2+} from the solution, but should not provide especially uniform particle size. In Fig. 6, the 6F material is seen to have both the finest particle size and a relatively gradual tailing off of the top of the sedimented column, symptomatic of a range of small particle sizes. The MacDermid process (5), on the other hand generates the sol with a Sn/Pd ratio of 2, and then adds stabilizing tin after the sol has formed. The result should be somewhat larger sol particles than those made by the Shipley process, but particles of a more uniform size limit. The centrifuging results in Fig. 6 confirm this; the upper level of the sedimenting column is relatively sharp for the 9070 bath.

Thus, particle size analysis of the commercial sensitizers, and our own experiments with particle size control, provide strong confirmation of our mechanism of particle size control in these colloid systems.

Summary and Conclusions

We have defined a number of processes in the Pd-Sn sol system:

1. The sol-generating reaction is initiated by the formation of a Pd-Sn complex.
2. The stoichiometry of the complex has been determined to be $Pd(II) \cdot 3Sn(II)$.
3. The complex is unstable and autoreductive, yielding a Sn-Pd alloy.
4. The sol particle size is determined by a layer of Sn^{2+}, which limits further growth.
5. The model developed here correctly predicts relative colloid particle size, both in our test solutions and in the commercial sensitizing baths.
6. The chemical processes occurring in the adhesion of the colloid to the sensitized surface have been described.
7. Chemical changes due to air oxidation of the bath have been described.
8. The colloid sedimentation rate has been determined.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1973 JOURNAL.

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