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NON-NOBLE COLLOIDAL CATALYSTS. (U)
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NON-NOBLE COLLOIDAL CATALYSTS

Surface Technology, Inc.
P.O. Box 2027
Princeton, New Jersey

May 1979



TECHNICAL REPORT AFML-TR-78-203
FINAL REPORT FOR PERIOD 15 MAY 1977 - 15 SEPT. 1978

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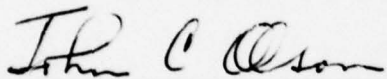
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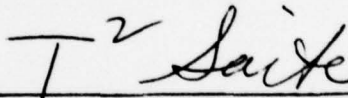
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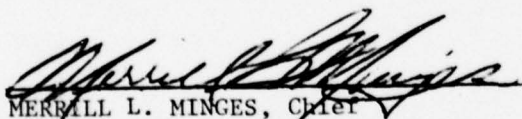


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FOREWORD

This report was prepared for the Electromagnetic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio by Surface Technology, Inc. of Princeton, NJ, under Contract F33615-77-C-5106, Projects ILIR/2423, Tasks ILIR00/242301, Work Unit Number ILIR0095 with John C. Olson, AFML/LPJ as the technical monitor. This research effort was supported in part by Director's Funds.

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SECTION 1

INTRODUCTION AND BACKGROUND

Although the electroless (autocatalytic) plating phenomenon is a relatively young technology¹, its merits and capabilities are well recognized in the field of metal finishing. The commercial adaptation of this metallization technique stems from the inherent advantages² as compared to electrolytic plating (electrodeposition). With the rapid growth of high technology during the past two decades, there are many products which are used by the consumer and the military in which electroless coating is an integral part of the manufacturing steps. Typical examples of products which employ electroless plating are printed circuitry and plated plastics parts. In the latter, products ranging from decorative parts to automotive parts are available. In recent years and particularly since the energy crisis of 1973, considerable interests and efforts are being devoted towards weight reduction for the purpose of energy savings. This interest is already noted in the increased use of plastics in automobiles as well as consideration of the potential uses of plastic in batteries.

Although these products are significantly different, certain common processing steps are applied to all. More specifically, the catalytic treatment of the plastic is an

essential step in providing a path for the initiation of the electroless plating process. The following key steps are found in common and are implemented in the sequence shown:

- 1 Surface conditioning (cleaning and etching) and rinsing.
- 2 Catalyzation treatment, accelerator, and rinsing.
- 3 Electroless plating (nickel, copper or cobalt).

A critical examination of the state of the art shows publications and issued patents to have advocated practices in which precious metals are used as the catalyst with specific attention focussed upon acidified tin/palladium compositions³⁻³⁴. It is interesting to note that references 18 through 34 in particular have focussed upon the fundamental aspects of palladium catalysts, and have constituted the basis for research during the past five years on commercial technology used since the early sixties. In spite of the many patents and publications citing improvements in catalytic behavior, most catalytic systems fall into either of the following basic categories:

- i Sensitization step (medium composed of SnCl_2/HCl) followed by an activation step (medium composed of PdCl_2/HCl), or
- ii Activation step (medium composed of $\text{PdCl}_2/\text{SnCl}_2/\text{HCl}$) followed by an acceleration step (medium composed of either dilute acid or alkaline compounds).

Although the palladium based catalysts are widely used in commerce, several limitations have been recognized throughout the years. These limitations are based upon:

- Pollution and personnel safety
- Materials and costs
- Product reliability

The following are just a few problem areas stemming from the present day catalysts.

1 Recently investigators have noted that certain printed circuit boards could not meet the mil-specification for insulation resistance. Analysis of the problem showed it to be directly correlated to the inclusion of high concentration of hydrochloric acid within the presently used palladium catalytic systems. The high acid content was believed to attack the glass fibers used in laminates. A partial solution for this problem was offered by the substitution of excess salt (NaCl) for the hydrochloric acid. However, this solution is only a compromise since in general it is highly desirable to process electronic devices with composition of low electrolyte concentrations.

2 The United States' prime source of palladium is the U.S.S.R.

3 Although there are many factors leading to the homogeneous decomposition of electroless plating baths, contamination of such baths with palladium is one major contributing source. In fact, analysis of plating baths shows an increasing content of palladium, along with decreased stability. This phenomenon has led to the development of a stability test devised through the measurement of the tolerance of electroless bath to added palladium^{35,36}. Decomposition of electroless plating baths results in significant problems with respect to waste disposal treatment as well as adding to the cost of operation.

4 In all present day systems, concentrated hydrochloric acid is used resulting in highly objectionable fumes. It is thus essential for proper personnel safety and for the prevention of equipment corrosion that highly effective ventilation be available.

5 Rinse water, especially that containing palladium, is generally not recirculated due to the fear of cross-contamination of the electroless plating baths with this palladium, thereby affecting bath decomposition.

6 In printed circuitry fabrication formaldehyde fumes are generally present since this component plays a major role in electroless copper formulations. At the same time, due to the

close proximity to hydrochloric acid fumes, a cancer-causing CME (chlorylmethyl methyl ether) may be formed thereby decreasing the personnel safety aspects of the operation.

7 Due to the chemistry of the stannous ions, special conditions, e.g., acidic media and additives, are present to minimize the oxidation and/or precipitation of tin.

8 Due to the lower overvoltage for hydrogen gas evolution on palladium it has been reported^{37,38} that reliability problems are encountered during the electrolytic plating resulting in excessive hydrogen gas evolution about the palladium and resulting in stressed deposits.

9 In the catalyzation of copper clad boards for printed circuitry, at times an 'over-catalyzation' phenomenon takes place resulting in poor adhesion. One cause for overcatalyzation is the relative position of copper and palladium in the E.M.F. series.

In recognizing the above limitations, Surface Technology has begun a pioneering effort toward the development of a new generation of catalysts. The objective set forth was the development of catalytic system(s) which would be applicable to printed circuitry processing and would be based upon non-precious metals (e.g., copper), and would operate at pH values close to neutral.

SECTION 2

OVERALL PROCESS STEPS

In the search for new catalytic systems various chemical concepts have been reported³⁹⁻⁴³. One of the primary points of distinction among these systems is whether the catalytic metal (e.g., copper) is part of a "true solution" or part of a "colloidal state". The concepts reported are generalized in the following process steps:

Catalytic solution approach^{39,40}

1. Contacting the non-conductor with a solution containing metal ions such as copper, nickel, iron, and cobalt.
2. Water rinse and/or drying.
3. Contacting the treated non-conductor with a reducing composition which is capable of reducing the metal ions on the non-conductor to the elemental catalytic state.
4. Electroless plating.

Catalytic colloidal approach⁴¹⁻⁴³

1. Contacting the non-conductor with a colloidal composition bearing a catalytic metal (e.g., copper) which may be in any of several oxidation states.
2. Water rinsing to remove excess colloid.
3. [Optional] Contacting the treated non-conductor with an activating composition which reduces the induction time for the metal being deposited. The

activating composition may be a reducing composition in the event that the colloid consists of metal ions in the positive (cationic) oxidation state.

4. Electroless plating.

While both of the above generic approaches are based upon sound chemical principles, the second approach is preferred because it envelops those properties and/or capabilities sought in a newly developed catalytic system which overcome the disadvantages recognized in the presently used palladium catalysts as outlined above.

Accordingly, the present program focussed upon improvements of the generic approach designated "catalytic colloidal approach". Specifically the approach taken was based upon the following compositions and key process steps.
[Water rinse steps are not here noted.]

Preferred catalytic colloidal approach

1. Contacting the non-conductor with a colloidal dispersion of copper where the copper may be part of an alloy, elemental state or an hydrous oxide.
Contact time of about 2 to 4 minutes used.
2. Treatment in an activation step, which is optional, and could be a dilute reducing medium, as to further activate the adsorbed colloid. Treatment time of about 2 to 4 minutes used.
3. Electroless copper plating.

In adapting the above process steps the induction time and metallic coverage were closely monitored during the plating step. Induction times for observed plating initiation were recorded along with the percent of the non-conductor which was coated with copper after 1-minute. In general, short induction times and 100% coverage were sought for the ideal system.

SECTION 3

COLLOID PREPARATION TECHNIQUES

Though there are several techniques⁴⁴⁻⁵¹ for the formation of colloidal dispersions, in the current program special attention was focussed upon the chemical precipitation method. In this method the insoluble phase (colloid) is nucleated through the chemical interaction of at least two reactants, e.g., copper ions with an hydroxide-bearing compound. This method was selected since it appears to lead to particles of different morphology⁴⁶, further leading to small particles.

These freedoms are highly significant and are a major asset to development of a practical catalytic system. Though most of the effort was conducted in the nucleation of copper colloid, with or without other metallic additives, the end product was varied depending upon the nature of the precipitating agent used to onset the colloid nucleation.

As seen in Table 1 the end product(s) and hence the ultimate properties, of the colloid are dependent upon various factors but mostly upon the chemical nature of the precipiating agent.

From survey of the state of the art for the preparation of colloidal dispersion utilizing the precipitation technique it appears that the colloidal states generally are nucleated through the interreaction of a liquid-liquid phase interreaction. For example, the precipitation of hydrous oxide colloids of copper are generally effected by a stream of alkaline material combined with a liquid phase containing a suitable copper salt. Similarly, the interreaction of a copper salt via a reducing agent (e.g., borohydride) is effected via a liquid-liquid interreaction. In the course of this effort it was conceived that there may be several advantages in effecting the formation of the colloidal phase by the interreaction of a gaseous reactant with a liquid phase as well as by gas-gas interreaction. Some of the anticipated advantages are:

1. The ability to disperse a gaseous product into a liquid may lead to a more finely divided colloidal product;
2. The interreaction via a gaseous reactant may provide the formation of more concentrated dispersions since the gaseous reactant does not lead to a dilution in volume;
3. The incorporation of a gaseous reactant into a liquid may also reduce additional ionic components which are present whenever a liquid reactant is used.
4. The nucleation of a colloidal product may lead immediately to a semi-dried product.

In an attempt to explore the merits of such an approach several experiments were conducted in which diborane gas along with nitrogen was used to onset the reduction of a copper solution to form a reduced admixture of colloidal copper and copper boride.

Though the experiment was effective, as of this date no major conclusion can be ascertained as to the effectiveness of the colloidal product derived by this approach, namely gas-liquid interreaction vs. a liquid-liquid interreaction. Several colloids prepared by the gas-liquid interreaction were found to be effective when used in the catalytic process.

Table 1

metal ions	precipitating agent	main colloidal product formed
copper	sodium hydroxide	hydrous oxide
copper	sodium borohydride	copper and copper boride
copper	dimethylamine borane	copper and copper boride
copper	hydrazine	copper

In the preparation of the colloidal dispersion it was found that best results were obtained by the reacting of a stream containing the reducing agent with the metal ions (copper) in the presence of at least one colloid stabilizer. This approach which is similar to chemical titrations has provided good control and reproducibility of the end product. Most of the nucleation reactions were carried forth above room temperature (approximately 50°C) in order to overcome any activation requirements. The amount of precipitating

agent required relative to the metal ions was found to be closely related to the calculated stoichiometric quantity required. Excess addition generally resulted in ultimate poor colloid stability. It was also noted that the rate of incorporation for the precipitating agent was a variant dependent upon its nature and the volume of colloid produced.

In order to improve upon the ultimate colloidal stability additional care was necessitated in order to maintain a low ionic strength for the final dispersion. To that end, it was found that monovalent anions (Cl^-) were preferred over divalent ions ($\text{SO}_4^{=}$), and that even among the anions, halides appear superior over others such as the nitrate anion.

SECTION 4

RESULTS AND DISCUSSION

Copper metallization is most commonly employed in the metallization of printed circuitry arrays. Accordingly, evaluation of the new catalysts in the present effort was made utilizing commercially available and widely accepted electroless plating compositions. Due to the autocatalytic nature of electroless plating it is evident that copper is a suitable catalyst for electroless copper plating initiation; hence, the major effort concentrated upon copper based catalysts. The choice of copper was also influenced by the great ease of stabilizing colloidal copper dispersions vs. cobalt and nickel types.

The following results represent highlights of the findings, particularly those results which have established improvements in performance of the catalytic colloidal catalysts.

A. Nickel or Cobalt Doped Copper Catalysts

Based upon discussions above, it is evident that copper does yield an effective catalyst for the electroless plating initiation, particularly for electroless copper plating. In the course of this activity it was observed that the manner by which nickel and/or cobalt are incorporated with the copper catalyst may be carried forth in one of two procedures.

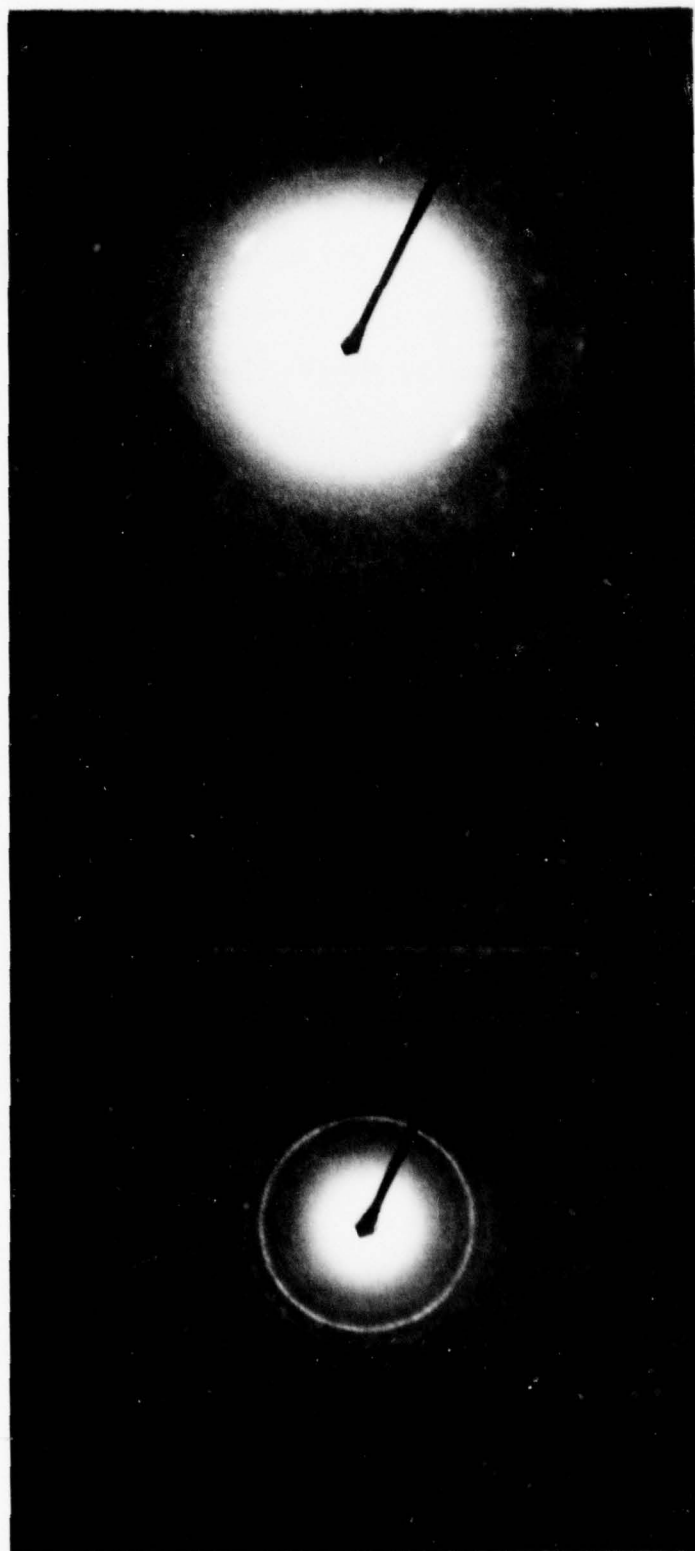
In the first procedure the nickel or cobalt is incorporated along with the copper prior to the nucleation of the colloidal phase. In this case the conversion reaction for the nickel and cobalt is similar to that of the conversion reaction of the copper, namely, if the copper is reduced so will the nickel and/or cobalt be reduced, especially if the reducing agent(s) used in the reaction are strong reducing agents which are derivatives of borohydrides-type. Therefore, in procedure No. 1 both the primary metal and the secondary metal used for doping are converted in a similar fashion.

The alternate procedure, procedure No. 2, which was found is to convert the primary metal, i.e., copper, to its final state via a reducing agent and thereafter add nickel or cobalt via the addition of a compound bearing the nickel ions. Though many experiments were conducted using these procedures, and though it was found that the incorporation of nickel and cobalt does enhance the catalytic activity in comparison to the same without their incorporation, the second procedure was

found most effective as a final catalyst, especially when nickel was used. In the second procedure the nickel is not converted by reduction, hence its apparent oxidation state is unchanged, unlike the change in oxidation state when procedure No. 1 is used.

However, in the course of the experiments it was found, particularly in the case of nickel, that the addition of the nickel compound after the copper colloid nucleation resulted in a catalytic activity significantly higher than those colloids resulting from procedure no. 1, as well as from the control (absence of any nickel or cobalt added). This observation seems to be more significant in the case of nickel rather than cobalt.

Electron microscopy techniques were utilized in an attempt to account for this observation. Colloids prepared by the above procedures were examined using the diffraction mode. Figures 1A vs. 1B show the diffraction patterns for procedures No. 1 and No. 2, respectively. It is evident that patterns resulting from the latter procedure reveal a greater amorphous character in comparison to the results of procedure No. 1. Hence, it is not surprising that the plating results or the activity of the catalyst is consistent with the degree of amorphous nature. Prior investigations related to palladium type catalysts have shown that in general the level of catalytic activity is related to the degree of amorphous nature. Generally



1B
Post colloid nucleation

1A
Prior to colloid nucleation

FIGURE 1

Incorporation of nickel with copper catalyst

speaking, in seeking the level of concentration for the nickel relative to copper it was found that less nickel is required as to yield the effect.

In an attempt to account for this unusual observation it is believed that the addition of the nickel compound after the copper colloid nucleation, which is generally above pH of 5 and lower than pH of 10, inherently yields the formation of some insoluble nickel hydroxide or hydrous oxide precipitation. The precipitated material would be deposited onto the previously nucleated colloid; hence, one may expect that the colloid containing the nickel after colloid nucleation will consist of a copper type nucleus with nickel precipitated about such nucleus. Furthermore, the presence of the nickel in the +2 valence along with the reduced copper apparently react electronically as to provide a catalytic state of higher activity.

B. Colloidal Stability and Colloidal Reactivity

Reactivity Modifiers

In the course of this research and development program it was recognized that the synthesized colloids must meet certain essential requirements: colloidal stability, and colloidal reactivity towards the electroless plating initiation process.

Colloid stabilizers are generally employed in meeting the requirement for colloidal stability. Generally speaking the colloid stabilizers are adsorbed onto the colloid nucleus; thereafter they are part of the colloidal double layer and the entire colloid entity. Therefore they are also present after adsorption of the colloid has taken place onto the dielectric substrate. Colloid stabilizers are generally materials which alone do not possess a catalytic activity in the initiation of the electroless plating process; hence, their presence on the substrate does not provide additional catalytic sites for plating initiation. For effective electroless plating initiation it is essential that the colloid nucleus or a precursor thereof must be available for a chemical interreaction with the electroless plating bath.

In the course of this research it was recognized that the act of colloid stabilization has generally resulted in diminishing the catalytic activity after the colloid is adsorbed onto the non-conductor. This observation was

anticipated since the act of stabilization introduces relatively inert chemical substance(s) which surround the colloid nucleus, and therefore provide a steric hindrance for the subsequent chemical reaction of the nucleus with a component of the electroless plating bath. Since both requirements must be met without any sacrifice of stability or reactivity, various efforts were attempted to deal with both.

In one approach it was thought that the highly stable colloids which are weakly active be adsorbed onto the non-conductor, and thereafter a portion of the colloid stabilizer be selectively removed exposing the colloidal nucleus to ensure high catalytic activity in the plating process. Though different chemical components were tried, the results were not encouraging. The main difficulty in this approach was the fact that the chemicals which were used to remove the colloid stabilizer from the surface were also removing the colloid nucleus, thereby diminishing the colloidal site distribution on the surface. This behavior is due to insufficient disparity in the selectivity of etchants towards the colloid stabilizer vs. the colloid nucleus.

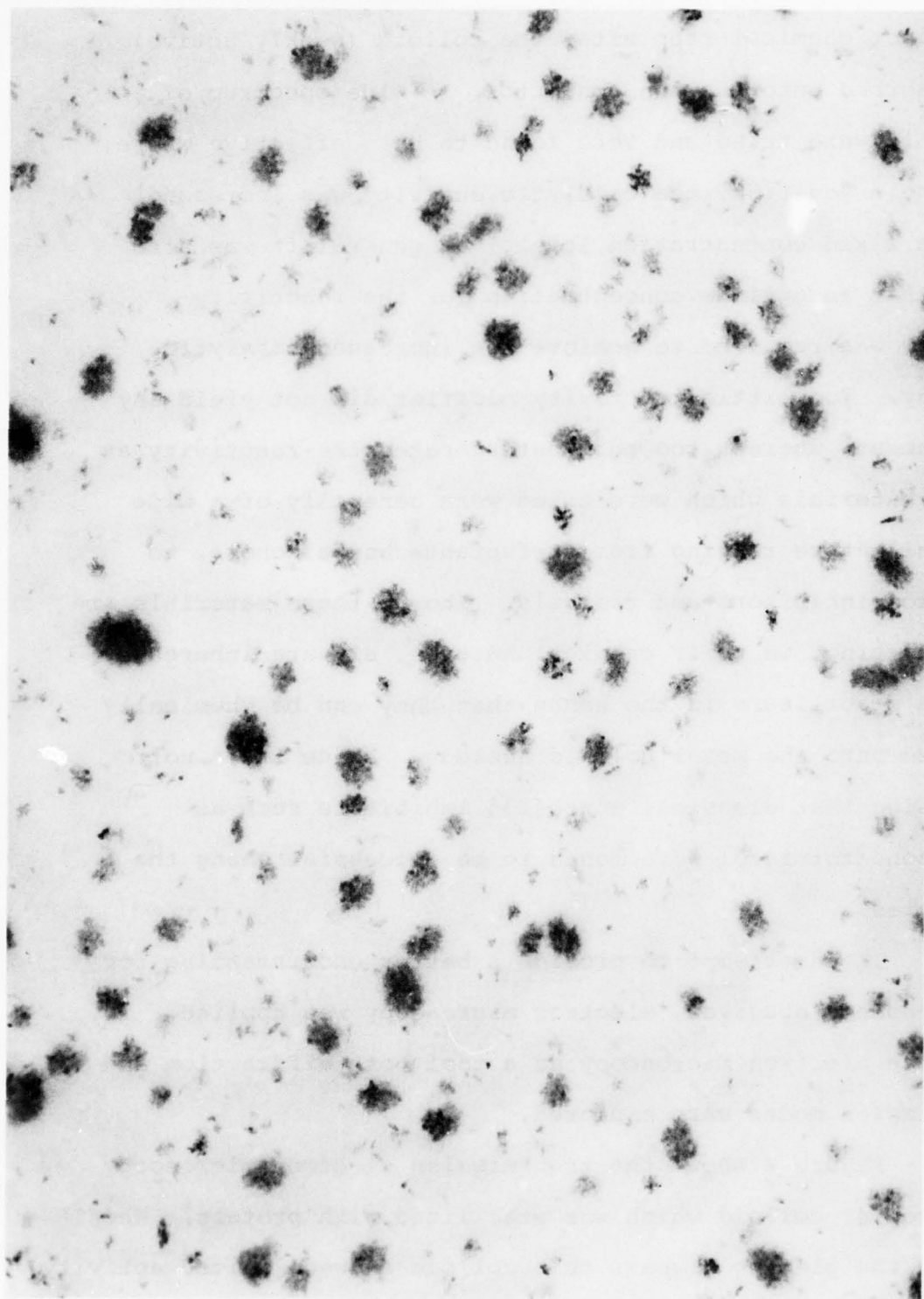
An alternate approach was used in which it was found that some of the colloids, though they are highly stable and weakly active, could be modified with the addition of materials coined as "reactivity modifier". The use of such material may be incorporated into the weakly active colloids or be used as

a distinct chemical step after the colloid (weakly active) was adsorbed onto the non-conductor. A wide spectrum of materials were tried and were found to be effective where, upon their addition, the catalytic activity was increased above a fixed concentration level. In general it was also found that an optimum concentration for the reactivity modifier was required to achieve the increased catalytic activity. Too little reactivity modifier did not yield any improvement, whereas too much deteriorated the reactivity as well. Materials which were tried were generally of a wide chemical nature ranging from surfactants and alcohols, to corrosion inhibitors and radicals. Though these materials are quite distinct in their chemical natures, all are inherently colloid stabilizers in the sense that they can be chemically adsorbed onto the metal colloid nucleus. Hence it is not surprising that classical corrosion inhibitors such as mercaptobenzotriazole were found to be successful among the candidates.

In an attempt to provide a better understanding for the phenomena observed, electron microscopy was applied. In using the electron microscopy as a tool both diffraction and transmission modes were explored.

Figure 2 shows the transmission electron microscopy for a copper colloid which was stabilized with protein. When used in the plating process this colloid showed limited activity.

FIGURE 2



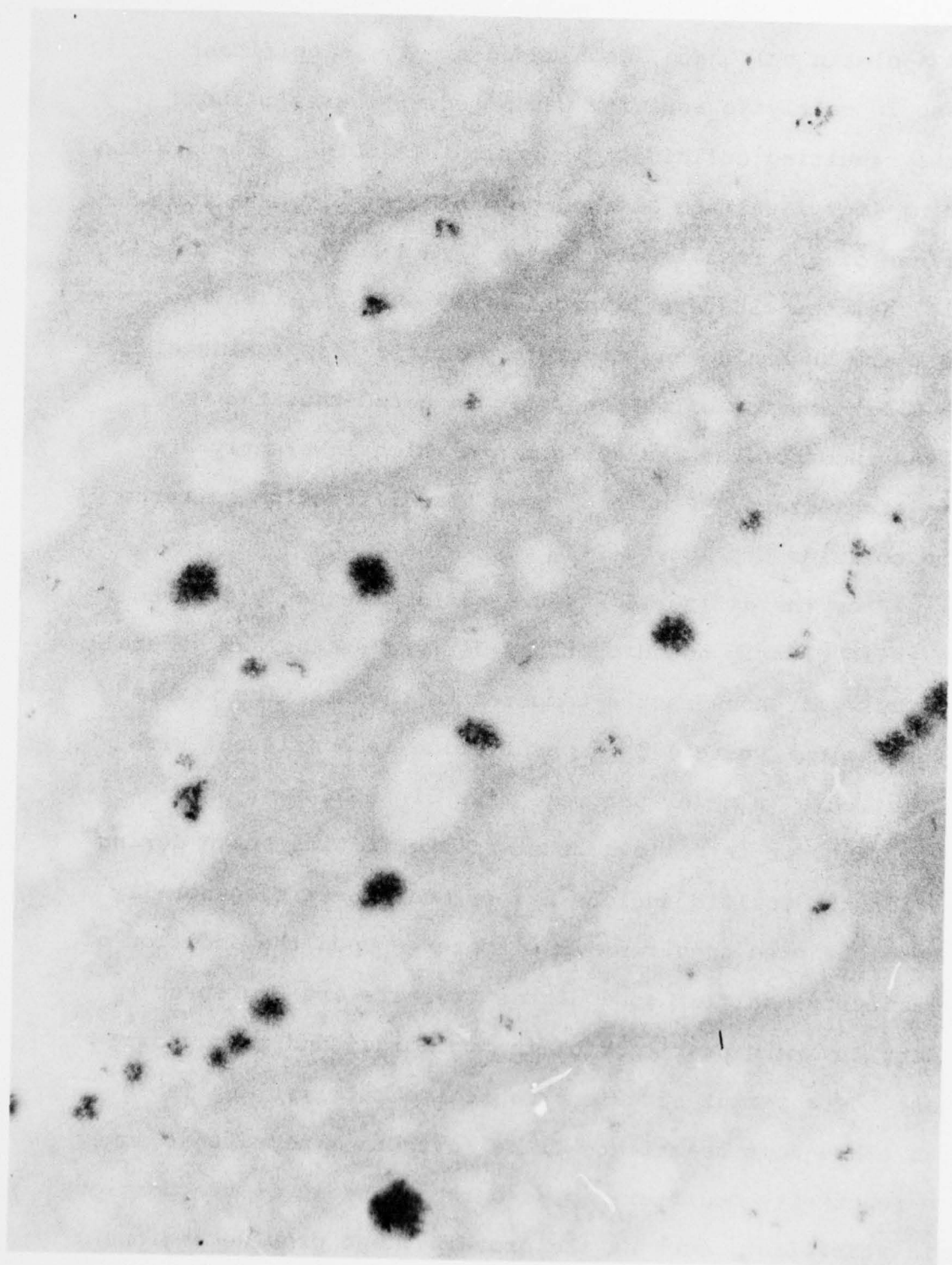
Transmission Electron Micrograph
for State "A" 1 cm = 670 Å

However, upon the addition of sodium lauryl sulfate (State B) and sodium α olefin sulfonate, each added singly, significant increase in catalytic activity was noted. Figures 3 and 4 show the resulting colloidal dispersio. after the incorporation of sodium lauryl sulfate and sodium α olefin sulfonate (State C). Comparison of the results of Figures 3 and 4 vs. Figure 2 (State A) reveals that the clusters (approximately 500 $\text{\AA}$ in size) in Figure 2 are broken up and discrete particles (approximately 50 $\text{\AA}$ in size) are formed instead. It is noted that the additives incorporated are surfactants which inherently are colloid stabilizers. Figure 5 shows the diffraction patterns for the colloids of Figures 2-4.

From the diffraction patterns for the newly derived states it is clearly noted that the derived states are generally of a higher amorphous nature compared to the starting weakly active colloidal state. This observation is consistent with the formation of a newer particle size distribution.

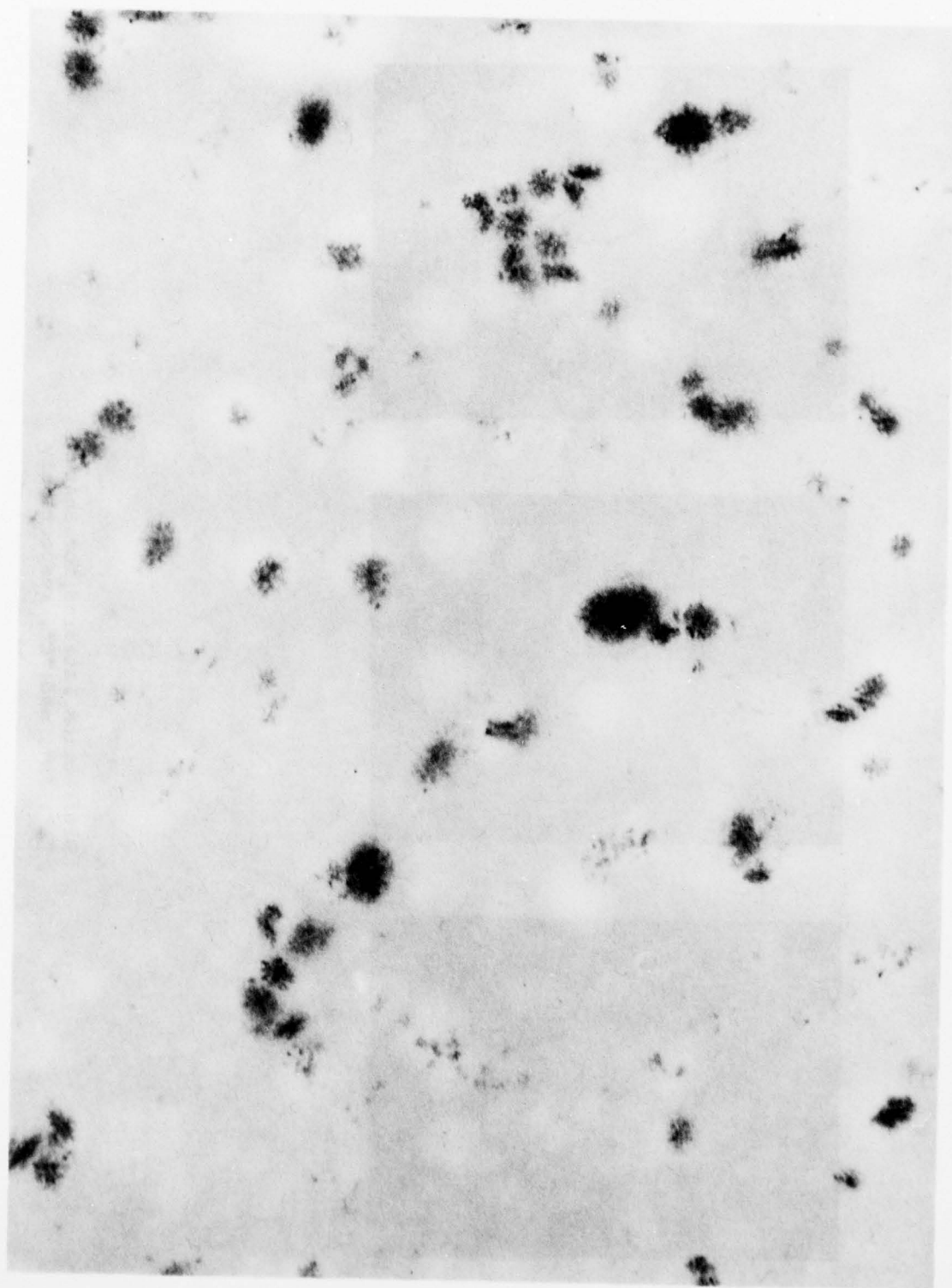
Thus, it is believed that in the initial state during nucleation the colloid nucleus has formed clusters, generally of several hundred angstroms in diameter. Upon the addition of the reactivity modifier some of the clusters are broken up providing discrete particles of the colloids, and in so doing increase the apparent surface area of the catalyst available for the subsequent reaction. It is further believed that some of the reactivity modifier may also replace some of the previous colloid stabilizer, such as the proteins, and provide regions

FIGURE 3



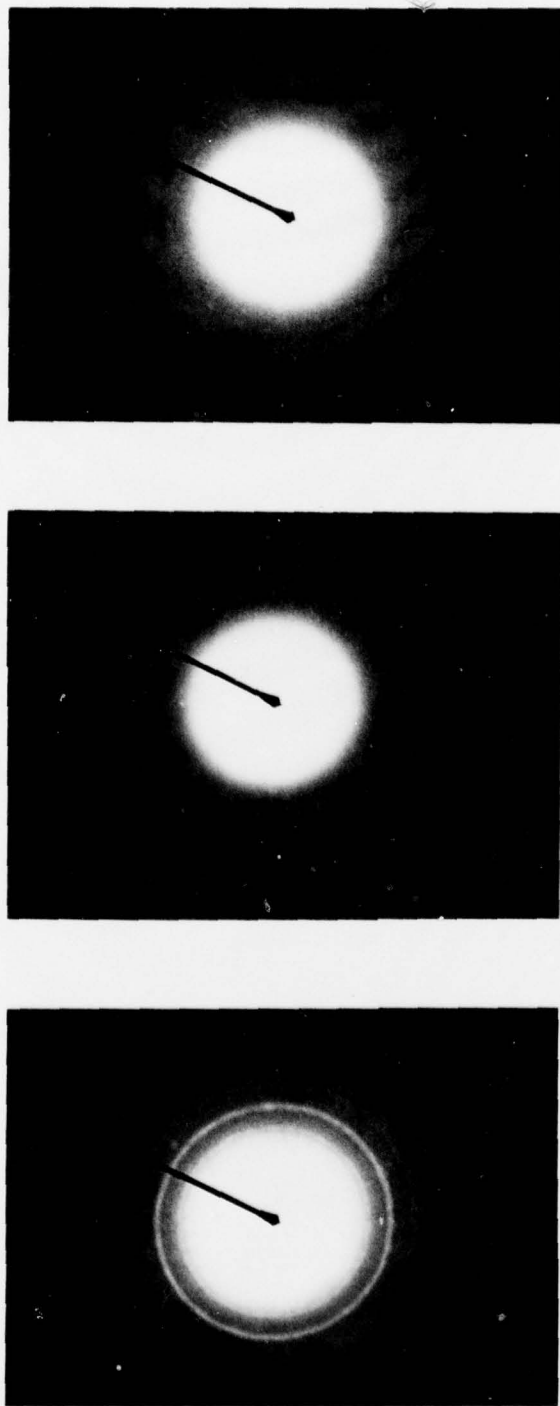
Transmission Electron Micrograph
for State "B"
1 cm = 670 Å

FIGURE 4



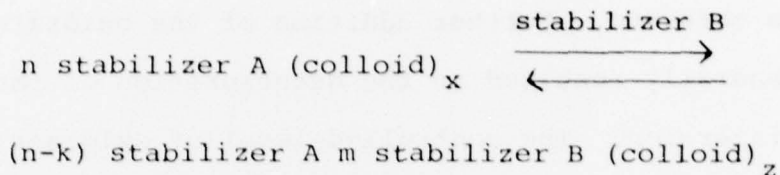
Transmission Electron Micrograph
for State "C"
1 cm = 670 Å

FIGURE 5



Diffraction Patterns for States
"A", "B", and "C", respectively

in which greater access can be made to the nucleus. In proposing this model the following schematic is provided showing the initial state and the derived state achieved.



where n, k, m, x, and z are some integer, and stabilizers A and B are distinct colloid stabilizers.

Controlled Oxidation

It has also been observed that certain colloids which are prepared by the reduction of copper with a reducing agent and to which materials like thiourea were added, were found to be inert, i.e., little plating if any was encountered. A typical composition used in the make-up of such colloid is:

CuCl ₂	0.04M
NiCl ₂	0.01M
NaBH ₄	0.039M
NaOH	0.196M
(NH ₂) ₂ CS	0.0067M
Orzan-S*	12.0 g/l
Final adjusted pH	8.0

*Dispersant - product of Crown Zellerbach Corp.

However, through the addition of a controlled concentration of an oxidizing agent a major increase in activity was observed. Further addition of the oxidizing agent has generally resulted in the deterioration of the colloidal dispersion. The controlled level of oxidizer incorporated was generally related to the concentration of thiourea present. It thus appears that the oxidizer appears to modify the colloid nucleus thereby resulting in a more active colloidal dispersion, and the thiourea is capable of stabilizing both the initial colloids as well as the modified state. Colloidal dispersions prepared and tested by this procedure were found effective for periods of up to 3 months.

C. Catalytic Boosters

Similar to the above section on nickel doped catalysts, it was found that compounds of metals, particularly those metals taken from the Periodic Table of the Elements of Periods IVB, VB, VIB, and VIIB, and Groups 4, 5 and 6, when incorporated along with the copper type colloids have caused enhancement of the catalytic activity in comparison to the same materials without the presence of such boosters. [Appendix A shows these elements of the Periodic Table of the Elements.]

It is also interesting to note that these materials are, at time, *more* effective when added post the copper colloid nucleation. Though it is not completely proven, it is believed that the mechanism for the catalytic enhancement is probably similar to the above model proposed with respect to nickel incorporation. Some of the elements used to boost the catalytic activity, such as manganese or chromium ions, are materials which could be readily precipitated to the hydroxide or hydrous oxide. Hence, their incorporation at pH's above 5 will cause the onset of their precipitation, and the precipitation takes place around the previously insoluble colloidal phase. Thereafter the enhanced activity is believed due to an electronic reaction between these transition metal ions and the copper based nucleus.

It is interesting to note that an inhibition effect is yielded when those transition metals to the right of copper (Group IB) on the Periodic Table of the Elements, for instance Group IIB, are incorporated into the catalyst in an ionic state. In other words, the level of catalytic activity tends to deteriorate particularly as the concentration for these metals (e.g., zinc, cadmium, mercury and the like) is increased. While the present findings are completely new in this field, in the chemical industry it has also been observed that copper catalysts used in hydrogenation reactions may be further activated by the addition of metals such as chromium, molybdenum, tungsten, etc. However, in the chemical industry the boosting metals are generally calcined and reduced to the elemental state, whereas the present observations have shown that the high oxidation states are effective (Cr(+3), Mn(+7), Mo(+6), etc.).

SECTION 5
CONCLUSIONS

The results of the present program have further reinforced prior research activities in this laboratory pertaining to non-precious metal catalysts for ultimate applicability to printed circuitry manufacturing. Though non-precious metals *alone* are not as good as the corresponding precious metals, particularly palladium, several findings of the present program have improved the performance of the former. This improvement in performance has resulted in catalytic activities which are virtually the same as the precious metal type currently used in commerce.

The observed improvements of copper based catalysts are:

1. *RELIABILITY* in synthesizing finely divided colloids.
2. *INCREASED ACTIVITY* by nickel or cobalt doping of the copper catalysts.
3. *INCREASED ACTIVITY* by the addition of reactivity modifiers which alter the steric configuration of the colloidal entity.
4. *INCREASED REACTIVITY* via controlled oxidation of the copper based colloids.

5. *INCREASED REACTIVITY* via the addition of catalytic boosters selected from metals of Period IVB, VB, VIB, and VIIB and Groups 4, 5, and 6 of the Periodic Table of the Elements.

The commercial implementation of colloidal compositions, particularly of non-precious metals, offers a realistic solution to problems encountered with presently used palladium type catalysts. The adaptation of these new catalysts will alleviate a wide range of problems from pollution and personnel safety, to materials, costs, and product reliability. Increased interest and confidence in this new technology by the *technical* community will positively influence its *commercial* assimilation.

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PERIODIC TABLE OF THE ELEMENTS

Table of Radioactive Isotopes

Isotopes occurring in nature are indicated by a natural number (half-life in parentheses) above the element symbol. All other isotopes are indicated by a mass number (half-life in parentheses) above the element symbol. The half-life of the isotope is indicated in parentheses after the mass number. The decay mode is indicated by a letter in parentheses after the half-life. The decay energy is indicated by a number in parentheses after the decay mode. The decay constant is indicated by a number in parentheses after the decay energy. The decay constant is indicated by a number in parentheses after the decay energy.

GROUP I A

GROUP II A

GROUP III A

GROUP IV A

GROUP V A

GROUP VI A

GROUP VII A

GROUP VIII A

GROUP IX A

GROUP X A

GROUP XI A

GROUP XII A

GROUP XIII A

GROUP XIV A

GROUP XV A

GROUP XVI A

GROUP XVII A

GROUP XVIII A

GROUP XIX A

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