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CATALYTIC GAS PLATING WITH NICKEL CARBONYL

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UNION CARBIDE NUCLEAR COMPANY
DIVISION OF UNION CARBIDE CORPORATION

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ABSTRACT

Exploratory studies have been made to determine the value of four potential catalysts in increasing the gas plating rate for nickel carbonyl. The catalysts studied were anhydrous ammonia, water vapor, oxygen, and hydrogen sulfide. No catalytic effect was observed for either ammonia alone or for water vapor alone. Oxygen was not tested alone. With hydrogen sulfide present in the 0.2 to 0.4% concentration range, significant improvement in plating rate was observed. The best results were obtained with mixtures of hydrogen sulfide and water vapor or mixtures of hydrogen sulfide and oxygen, using hydrogen sulfide concentrations of 0.2 to 0.8%, water vapor concentrations of 0.03 to 0.08%, and oxygen concentrations of 0.8 to 1.0%.

The catalytic effect can also be used to reduce the temperature required for gas plating with nickel carbonyl. Using the hydrogen sulfide-oxygen mixture, nickel carbonyl gas plating was performed at room temperature on the following materials: iron, copper, aluminum, glass, paper, cardboard, cotton cloth, and cork.

CATALYTIC GAS PLATING WITH NICKEL CARBONYL

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CATALYTIC GAS PLATING WITH NICKEL CARBONYL

SUMMARY

In the conventional gas plating process, an inert carrier gas containing greater than 4% nickel carbonyl flows across the heated material being plated. When nickel carbonyl strikes the hot surface, it thermally decomposes, depositing nickel and generating carbon monoxide as a reaction product. The operating temperature is usually above 140°C. to obtain adequate plating rates, but it must be kept below 200°C., and preferably below 180°C., to avoid high carbon concentration in the plate.

A series of scoping studies was performed to determine if the plating rate could be increased by use of catalysts. A conventional laboratory-scale gas plating system was modified to study catalytic plating of 6-inch sections of 1/2-inch IPS iron pipe. The Reynolds number of the plating gas, 20% nickel carbonyl in a carbon dioxide carrier, was 380 which was high enough in the laminar region to avoid powder formation in the gas stream. These studies covered the temperature range from 100 to 180°C.

No improvement in plating rate was observed when either water vapor or anhydrous ammonia was added to the plating gas. In fact, a reduction in rate was observed. Oxygen alone was not evaluated. When hydrogen sulfide was used at the 0.2 to 0.4% level, a significant increase in plating rate occurred. Even better results were obtained with mixtures of hydrogen sulfide and water vapor or hydrogen sulfide and oxygen. For hydrogen sulfide concentrations of 0.2 to 0.8%, water vapor concentrations of 0.03 to 0.08%,and oxygen concentrations from 0.8 to 1.0%, the plating rate was increased by at least a factor of three between 100 and 150°C. The data indicated that the plating rate may be a function of catalyst concentration.

The catalysts can also be used to reduce the plating temperature. For instance, conventional plating would have to be performed at 150°C. to produce the plating rate obtained with the hydrogen sulfide-oxygen catalytic mixture at 100°C.

Where the plate produced by the conventional process was slightly rough and dull, but ductile, the plate produced by the catalytic process was smooth and shiny, but brittle. In either case, good mechanical bonds were obtained, and diffusion bonding was produced by heat treatment in hydrogen for 1 hour at 800°C. Microscopic examination of the catalytic plate revealed occasional cracks or porosity which did not penetrate the film and infrequent crystalline inclusions, probably nickel sulfide. Analysis of a typical sample of the plate showed 0.62% sulfur, 0.17% oxide, and 0.002% carbon.

A two-step process was developed to combine the best properties of the conventional and the catalytic plates. The conventional plating process was used first; then, the catalytic plating was employed to yield a smooth, shiny surface.

A series of exploratory runs was made at room temperature. No plating occurred without catalysts. Hydrogen, ammonia, and hydrogen sulfide catalyzed the plating reaction, but the best results were obtained with a mixture of 0.4 to 0.7% hydrogen sulfide and at least 10% oxygen. The following materials were plated: paper, cardboard, cork, glass, iron, copper, and aluminum. The plating rate was low, estimated 0.3 mil/hr., so the potential uses of the room temperature process are probably for the application of decorative coatings to materials which cannot be handled at higher temperatures or for the application of conducting coatings to nonconducting materials to permit them to be electroplated.

It should be emphasized that a limited series of scoping tests was performed. Additional studies would be needed to establish quantitative relationships for key process variables.

INTRODUCTION

In gas plating or vapor plating, the terms are used interchangeably, nickel in the form of its carbonyl compound is brought in contact with the heated article to be plated. The nickel carbonyl undergoes thermal decomposition, forming a nickel plate on the article and giving off carbon monoxide in the process. For some speciality jobs, the gas plating is done with the pure nickel carbonyl vapor; however, this requires operation below atmospheric pressure which is not so desirable from the safety standpoint as operating above atmospheric pressure. In most applications, an inert gas, such as carbon dioxide, nitrogen, or hydrogen, is used to carry the nickel carbonyl vapor to the article being plated. Turbulent flow is normally employed to avoid powder formation in the gas stream and to provide good mixing between the gas and the work. The nickel carbonyl concentration is usually in the 4 to 25% range, while the plating temperature is normally in the range of 140 to 180°C. Below 140°C., the plating rates are low. Above 180°C., the carbon content of the plate increases because the carbon monoxide reaction product breaks down, forming carbon and carbon dioxide.

In his book, Powell (1) describes the nickel carbonyl vapor plating process in more detail; Croxton (2) and Hoover (3) have prepared bibliographies on the properties of nickel carbonyl.

This report describes an exploratory study of four potential catalysts: anhydrous ammonia, water vapor, oxygen, and hydrogen sulfide. Most of the plating work was done on heated sections of 1/2-inch iron pipe. Also included in the report is an account of room temperature plating tests using articles which cannot be subjected to the higher temperatures required in the conventional gas plating process.

EXPERIMENTAL

MATERIALS

Nickel Carbonyl

Much of the nickel carbonyl used in these studies was a commercial product obtained from the Matheson Company in 25- or 50-pound cylinders. Some of the nickel carbonyl was prepared in this laboratory by reacting nickel prepared by the carbonyl process with carbon monoxide at 150 to 200 psig. and 60 to 100°C.

The liquid nickel carbonyl was not analyzed. Instead, analyses were performed on nickel mirrors formed when nickel carbonyl vapor contained in a carbon dioxide carrier was passed through clean, dry, glass tubes, heated to 150°C. Analytical results are presented in table I. The metallic impurities were determined by qualitative spectrochemical analysis, accurate to a factor of 3. Sulfur was determined iodimetrically to a precision of ± 0.001%, the limit of detection being 0.001%.

TABLE I

TYPICAL ANALYSES OF NICKEL FORMED BY THE THERMAL DECOMPOSITION OF NICKEL CARBONYL

	Impurity Concentration, %	
Element	Matheson Nickel Carbonyl	ORGDP Nickel Carbonyl
Calcium	0.0003	0.0002
Copper	0.00005	0.00005
Iron	0.02	0.003
Magnesium	0.0003	0.0004
Silicon	0.0002	0.0003
Sulfur	<0.001	<0.001

As shown in table I, the only significant difference noted between the Matheson nickel carbonyl and the ORGDP nickel carbonyl was in iron content. The iron was probably present as iron carbonyl. The fact that two carbonylation reactions were employed would account for the higher purity of the carbonyl produced in this laboratory. The other metallic impurities were probably present as fine metal or oxide particles. From the standpoint of the catalytic studies, it is significant that sulfur was not detected in either material.

Other Reagents

Four potential catalytic reagents were employed in these studies: ammonia, hydrogen sulfide, water, and air. The anhydrous ammonia was a commercial product obtained as a liquefied gas from the Matheson Company. The manufacturer's specifications called for a purity of greater than 99.95%, the major contaminants being water, oil, and noncondensable gases. The moisture content was less than 50 ppm., and the oil content was less than 5 ppm.

The hydrogen sulfide was also obtained from the Matheson Company as a liquefied gas. The manufacturer's specifications called for a minimum purity of 99.5%, typical impurities being carbon disulfide, carbon dioxide, methyl mercaptan, carbonyl sulfide, and sulfur dioxide.

The distilled water used in these studies had a maximum impurity level of 60 ppm. It was boiled prior to use to evolve dissolved oxygen.

Compressed air used as a source of oxygen had been processed through activated alumina dryers. The frost point of this air was below -50°C.

Carrier Gases

The carrier gas for the nickel carbonyl was Matheson commerical grade carbon dioxide. The manufacturer's specifications are as follows: carbon dioxide, 99.5% minimum; nitrogen, 0.342% maximum; oxygen, 0.086% maximum; and water, 0.072% maximum.

The nitrogen used as a carrier gas for the water vapor catalyst was prepared by the evaporation of Linde liquid nitrogen. It contained a maximum of 50 ppm. oxygen and had a frost point of less than -70°C.

Test Sections

Most of the plating studies were performed on 6-inch threaded sections of 1/2-inch IPS, schedule 40, iron pipe. The following cleaning procedure was employed routinely:

a. Soak for 3 to 7 minutes at 88 to 93°C. in a 52 g./l. solution of Oakite No. 66.

b. Cold running water rinse for 30 to 60 seconds.

c. Pickle for 10 minutes in 50% by volume hydrochloric acid at 21 to 32°C.

d. Cold running water rinse for 30 to 60 seconds.

e. Neutralize for 30 to 60 seconds at 21 to 32°C. in an aqueous solution containing 11.2 g./l. sodium hydroxide and 3.7 g./l. sodium carbonate.

f. Cold running water rinse for 30 to 60 seconds.

g. Hot running water rinse for 30 to 60 seconds at 88 to 93°C.

h. Dip in dry acetone at room temperature for 10 to 30 seconds, followed by air drying.

APPARATUS AND INSTRUMENTATION

Flow Circuit

The catalytic gas plating system is shown schematically in figure 1. After passing through the rotameter, the carbon dioxide carrier gas is bubbled through liquid carbonyl in the saturator and then passed through two mist separators in series. The saturator and the mist separators were immersed in water-ice baths. After addition of metered amounts of catalysts, the carbonyl-containing gas was passed through the 6-inch test section of 1/2-inch iron pipe which was heated by a tube furnace. The unreacted carbonyl was then burned, and the combustion products were vented. For safety, the entire apparatus was operated in a closed fume hood.

Materials of Construction

Most of the apparatus was constructed from 3/8-inch copper tubing. Permanent connections were silver-soldered, while SAE flare fittings were used for connections which had to be broken frequently during the course of the work. The pipe fittings on the 6-inch test section were pretinned with soft solder to produce leak-tight joints. Hoke 413 valves were used throughout the system, either as control valves or as block valves. These needle valves had welded diaphragms which avoided leak problems.

Saturator and Mist Filters

The construction of the saturator and the mist filters is shown in figure 2. The shell of the saturator was 1-5/8-inch o.d. copper tubing. The carrier gas entered through a central tube which was sealed at the bottom, so the carrier gas was forced out through thirty 1/32-inch holes drilled at random in the bottom 2 inches of the tube. The thermocouple well was used to determine when the temperature of the liquid carbonyl had reached equilibrium with the surrounding water-ice bath. The pressure vacuum gage was used when filling the saturator or for detecting build-up of carbon monoxide pressure when the saturator was stored between experiments. The mist filters were of similar construction, except that they were filled with copper wool to remove entrained droplets of nickel carbonyl from the carrier gas.

Flow Measurements

The carbon dioxide flow was measured with a Fisher and Porter rotameter having a rated capacity for carbon dioxide of 0 to 1 cfm. Catalyst flows were determined with Fisher and Porter rotameters, rated 0 to 100 cubic centimeters per minute for air. Using air at 25°C. and a system operating

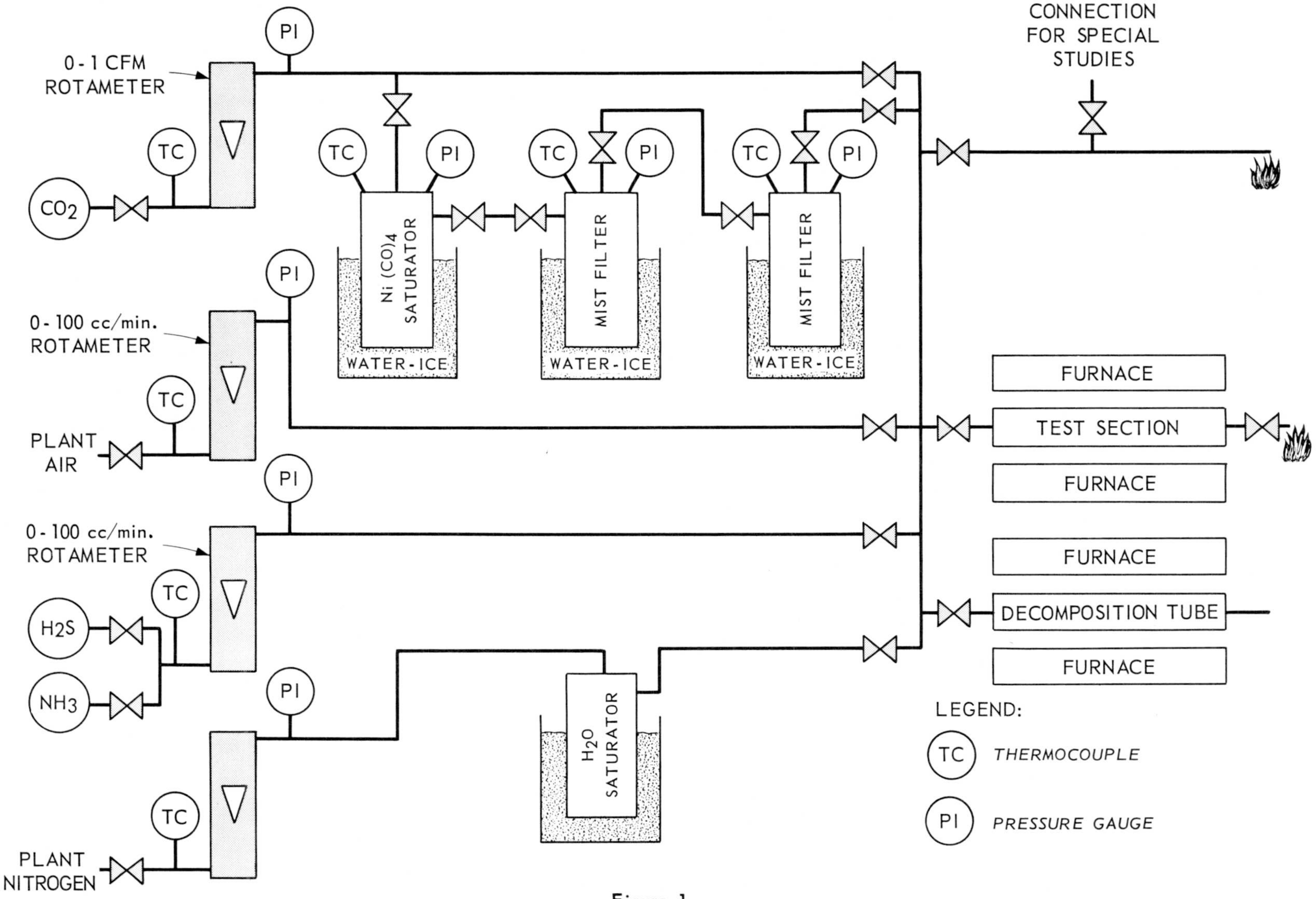
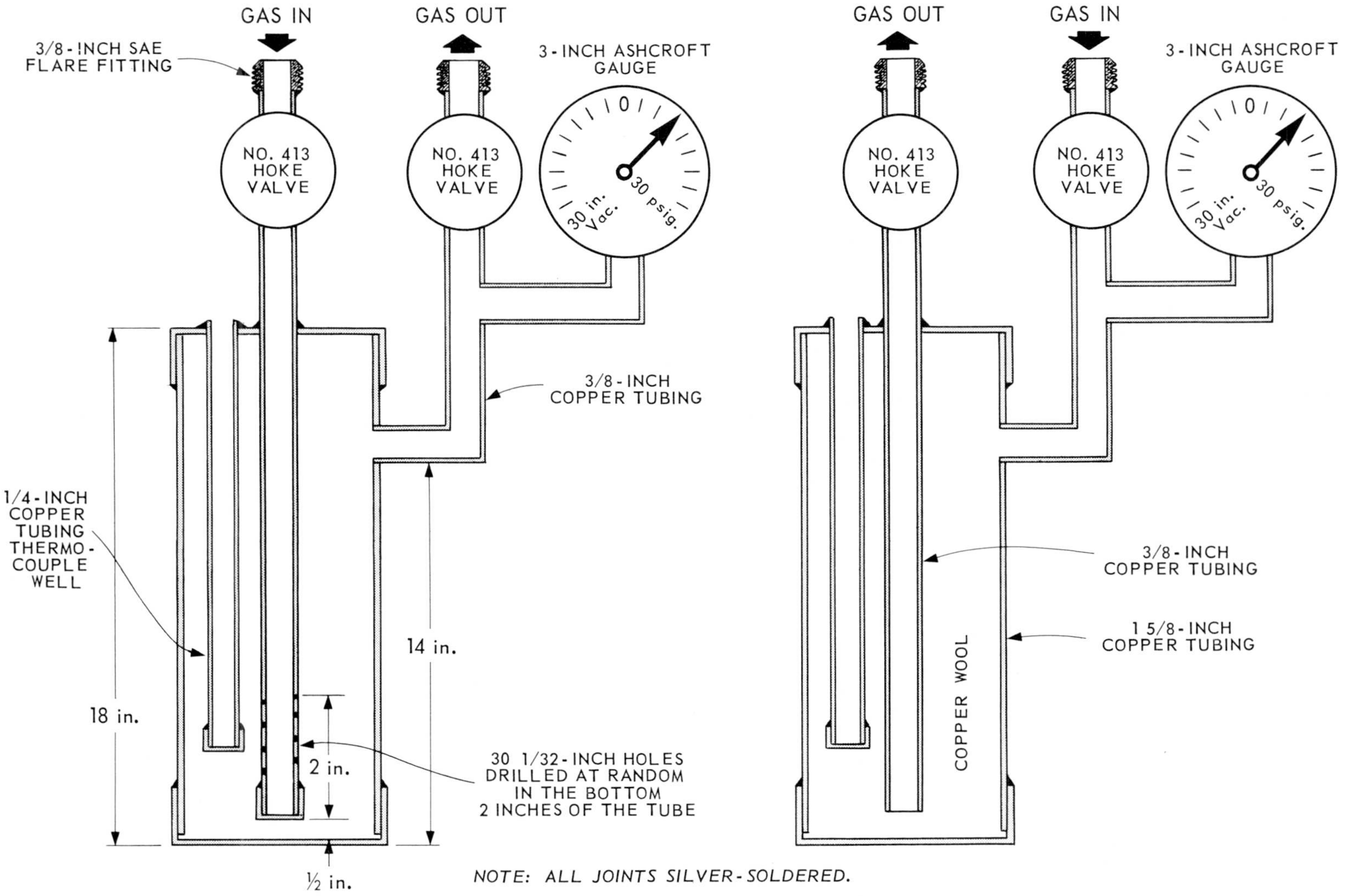


Figure 1
CATALYTIC GAS PLATING SYSTEM



NOTE: ALL JOINTS SILVER-SOLDERED.

NICKEL CARBONYL SATURATOR

NICKEL CARBONYL MIST FILTER

Figure 2
NICKEL CARBONYL SATURATOR AND MIST FILTER

pressure of 2 psig., the carbon dioxide rotameter was calibrated against standard critical orifices which were accurate to ± 0.5%. The catalyst rotameters were also calibrated with air at 25°C. and 2 psig. against positive displacement flasks accurate to ± 0.5%. Theoretical computations(4) were used to convert the calibrated air flow to the flow of the carbon dioxide carrier gas or the catalysts and to correct for variations in operating temperature and pressure. Operating temperatures for the rotameters were measured with copper-constantan thermocouples which were silver-soldered to the copper tubing immediately upstream from the rotameter. The operating pressures were determined with 3-inch, 0 to 15 psig., Ashcraft, bourdon-tube, pressure gauges, attached at the outlet of the rotameters.

No leakage problems were encountered with the rubber gaskets used to connect the glass rotameter tube to the metal rotameter casing. Permatex No. 2 sealing compound was employed to obtain a leak-tight fit between the system piping and the pipe-thread connections on the rotameter casing.

Temperature Measurement and Control

For all temperature measurements, silver-soldered copper-constantan thermocouples were employed. The calibration of each thermocouple was checked at the melting and boiling points of distilled water, while the output of thermocouples was measured on a Rubicon No. 21017 potentiometer to an estimated precision of ±0.5°C.

The 1/2-inch pipe test sections were enclosed in a resistance-heated tube furnace. Temperature control was manual through the use of a Variac to regulate the voltage supplied to the furnace heating element. The maximum variation in temperature during the course of a 1-hour test run was ±5°C.

Thermocouple probe studies showed variations in temperature of as much as 15°C. along the pipe, with the most pronounced differences near the ends. Probe studies around the pipe showed a maximum variation of 2°C. The problem of longitudinal temperature variations was avoided by studying the gas plating process in a 1-inch zone at the center of the pipe. Thermocouples were embedded in slits cut half way through the pipe wall at each end of this 1-inch zone and were held in place by soft solder or Sauereisen cement. The maximum temperature variation between these two locations during the course of a 1-hour experiment was 2°C.

Gas Analyses

At the start and end of each plating run, the saturator and the mist filters were weighed. From the change in weight and the flow rate of the carbon dioxide carrier gas, the average concentration of nickel carbonyl in the carrier gas was calculated.

A second analytical technique was used to obtain a quick measurement of carbonyl concentration at the start of each run. For the first 60 seconds, the gas flow was diverted from the test section to a decomposition tube heated to 150°C. The details of this decomposition tube are shown in figure 3. Visual examination indicated that the nickel carbonyl entering the tube was decomposed. Analyses of the nickel mirror formed in the tube demonstrated that the purity was sufficiently high, 99.8%, that the nickel carbonyl concentration could be based on the weight of the nickel deposit. The decomposition tube was attached to the system with a standard ground-glass tapered seal, using Apieazon M stopcock grease. The grease was dissolved off with trichlorethylene prior to weighing.

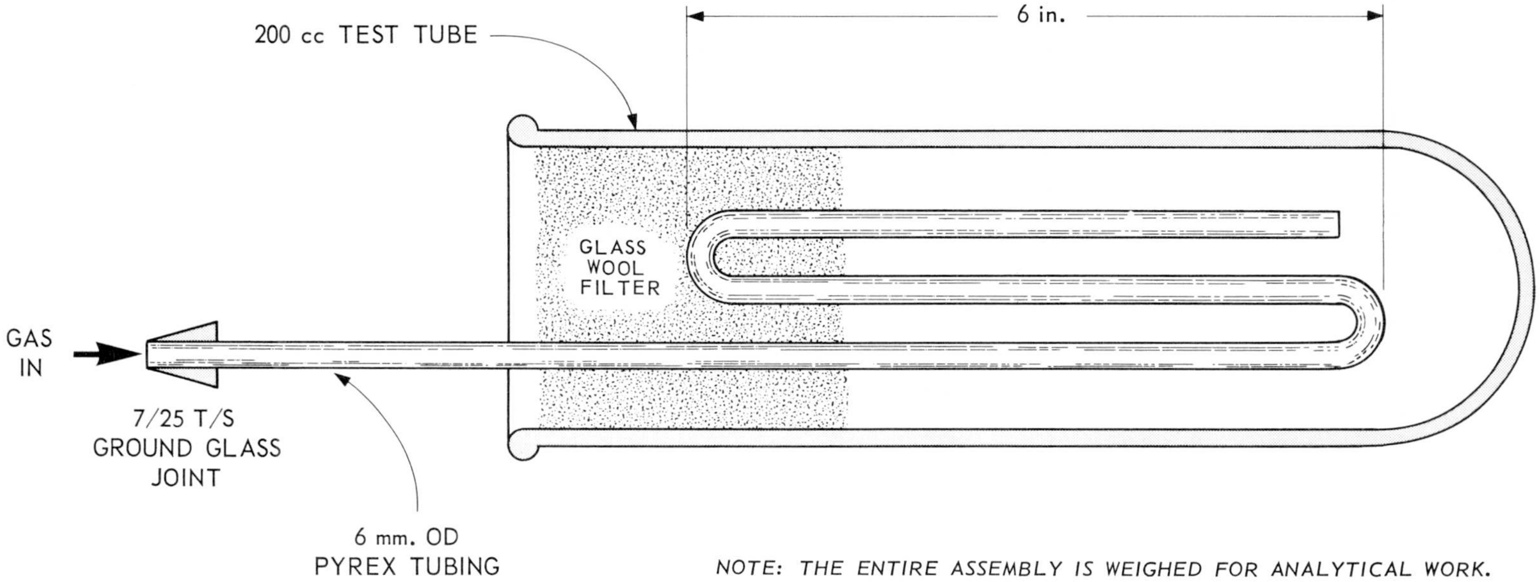
The concentrations of ammonia, hydrogen sulfide, and oxygen catalysts in the plating gas were calculated from flow measurements. The flow rates of nitrogen saturated with water at either zero or 25°C. were employed to determine water concentrations in the plating mixture.

PREOPERATIONAL PROCEDURE

The system used to fill the saturator is shown in figure 4. The saturator and the source cylinder of nickel carbonyl were attached to the system, and all connections were made leak tight. With both valves of the saturator and the valve on the source cylinder closed, the system was evacuated and then pressured with nitrogen to 5 psig. The evacuation and pressuring operations were repeated four times to remove all traces of oxygen from the system.

The next step was to "top" the nickel carbonyl cylinder, i.e., to remove carbon monoxide which might have built up during storage of the cylinder; carbon monoxide would interfere with the vapor transfer of the nickel carbonyl from the cylinder to the saturator. After closing the valves on the saturator and the vacuum pump, the valve on the carbonyl cylinder was opened slowly, and the mixture of nickel carbonyl vapor and carbon monoxide was allowed to expand into the surge volume, at all times being careful not to exceed the safe operating pressure of 10 psig. After closing the cylinder valve, the gas in the surge drum was slowly evacuated through the hot decomposition tube. This procedure was repeated until the pressure in the surge drum, with the cylinder valve open, did not exceed the vapor pressure of nickel carbonyl at the cylinder temperature by more than 1 psi.

After closing the cylinder valve, the material in the surge volume and piping was evacuated, and the valve to the pump was closed. The valve on the side of the saturator was opened, as was the valve on the carbonyl cylinder, and the vapor transfer was begun. When sufficient material had been transferred as estimated by the position of the frost line on the side of the saturator, the valve on the cylinder was closed, and the valve on the saturator was allowed to remain open long enough to remove most of the carbonyl in the surge volume and piping by thermal pumping. The valve on the side of the saturator was then closed, and the carbonyl in the lines and surge volume was evacuated through the decomposition tube. The entire unit, including the saturator and the carbonyl cylinder, was then pressured



NOTE: THE ENTIRE ASSEMBLY IS WEIGHED FOR ANALYTICAL WORK.

Figure 3
NICKEL CARBONYL DECOMPOSITION TUBE

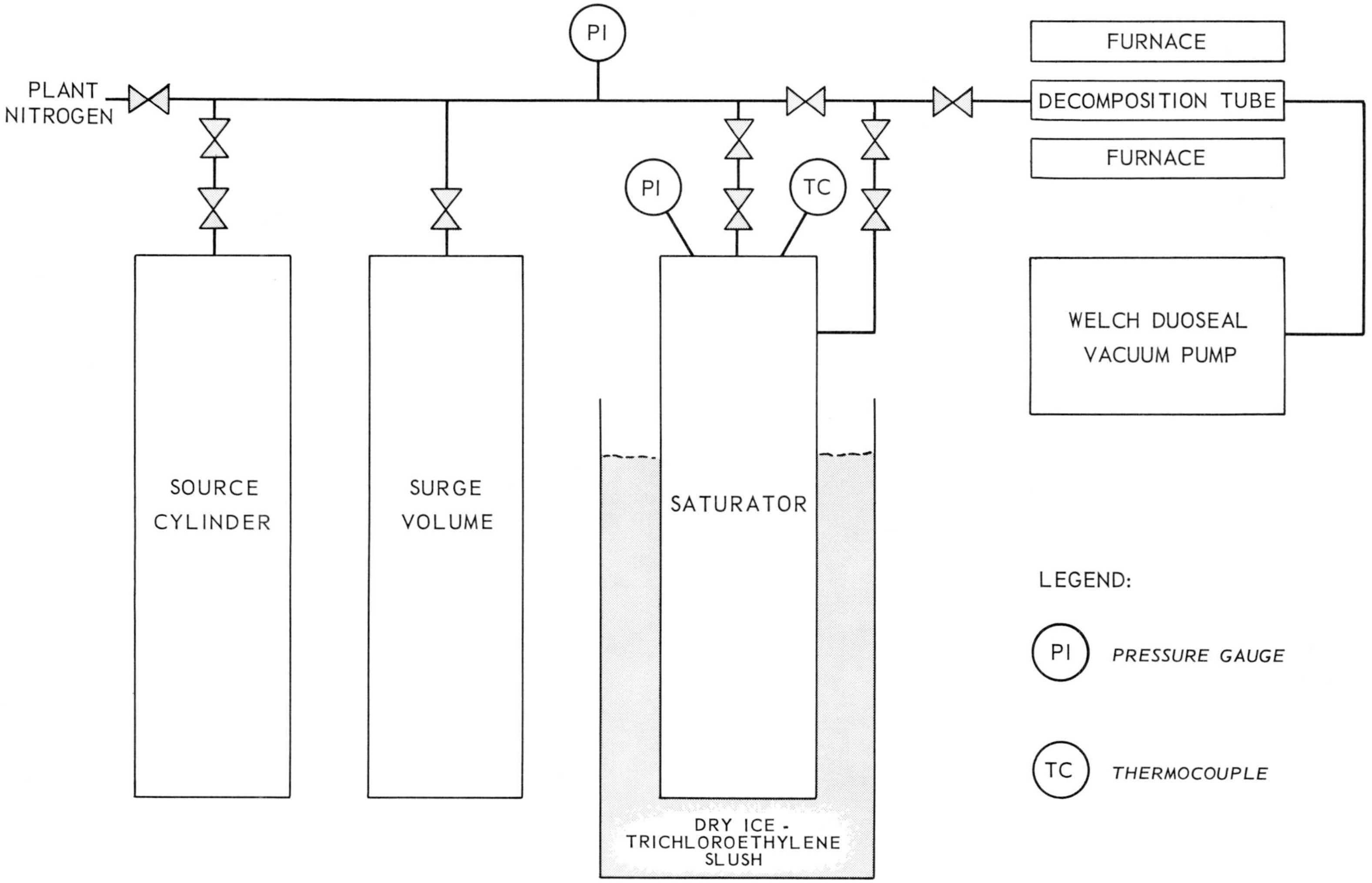


Figure 4
SYSTEM FOR CHARGING THE SATURATOR

to 2 psig. with nitrogen to prevent inleakage of air. Following this, the saturator and source cylinder were valved off, and the lines and surge volume were subjected to at least 5 repetitive pressuring and evacuation operations to remove the last traces of nickel carbonyl. The carbonyl cylinder and the saturator were then removed from the system. For safety, the entire operation was performed in a hood.

LEAK TESTING

When the saturator and test section were in place on the gas plating system, figure 1, the following leak testing procedure was employed. First, the system was pressured to 10 psig. with carbon dioxide, and all new connections were tested with a soap suds solution. When no further leaks could be detected, the carbon dioxide cylinder was valved off from the system, and an outleakage rate was measured. No detectable pressure change on the bourdon gauges in 30 minutes was considered an acceptable outleakage rate. As a final leak test, a small flow of carbon dioxide was passed through the saturator to spread a low concentration of nickel carbonyl through the system, which was then pressured with carbon dioxide to 10 psig. The outside of the system was then tested with a hydrogen flame for outleakage of nickel carbonyl. Any carbonyl present shows as white coloration in the colorless hydrogen flame. This was the final criterion for leak tightness. The system was considered ready for operation when it had been made leak tight, when it had been thoroughly purged with carbon dioxide, and when the test section was at the desired temperature.

PLATING OPERATIONS

At the start of the run, the carbon dioxide was by-passed around the saturator and mist filters until the desired flow rate had been established. Then, the carrier gas flow was diverted through the saturator and mist filters and into the decomposition tube for 1 minute to check the nickel carbonyl concentration. Next, the carrier gas containing the nickel carbonyl was passed through the test section, and immediately afterward, the flow of catalyst was started at the desired level. The gases leaving the test section were burned, and combustion products were vented through the hood.

Temperatures, pressures, and flow rates were measured and adjusted at 5-minute intervals. Aural tests were also made every 5 minutes to determine if the carrier gas was bubbling through the liquid carbonyl in the saturator. In run 1, where bubbling stopped early in the run because the saturator was low in nickel carbonyl, a marked reduction in carbonyl concentration occurred as shown in table II. At the end of the run, the saturator and mist filters were valved closed, and carbon dioxide was passed through the by-pass and through the test section to purge the system of nickel carbonyl. At the end of the test, the exit gases were tested in a hydrogen flame to make sure that the system had been adequately purged. After removal of the test sections, the entire unit was pressured to 5 psig. to prevent oxygen inleakage.

EVALUATION METHODS

Microscopic Examination

A 1-inch section was cut from the center of each plated pipe; i.e., between the thermocouples. This section was then cut in half. One half was used for microscopic examination,and the other half was reserved for corrosion testing.

The 1/2-inch section was mounted in Bakelite plastic, and the side which would have been in the exact center of the pipe was polished and examined metallographically for porosity, cracks, inclusions, and bonding. The thickness of the plate was determined in three locations near the top of the plate where the temperature had been measured. The estimated precision for the average thickness of the plate was ±0.1 mil.

Corrosion Tests

The other 1/2-inch section was immersed in a 1% aqueous sodium chloride solution for 1 hour at 95°C. After drying, the test section was split and examined for rust.

SAFETY PRECAUTIONS

Safety Problems in the Use of Nickel Carbonyl

Nickel carbonyl is a dangerous material. The liquid and high concentrations of the vapor burn spontaneously in air; furthermore, spilling liquid carbonyl in air will lead to an explosion. When nickel carbonyl and oxygen are mixed in a closed container, an explosion may also occur. This is apparently a chain reaction process, and the explosion will occur after an indeterminate period which depends on concentrations and the geometry of the apparatus. Breathing high concentrations of nickel carbonyl vapor can be fatal, while prolonged exposure to low concentrations of nickel carbonyl vapor can lead to sinus cancer. At the time this work was done in 1949 to 1950, the accepted Threshold Limit for nickel carbonyl was 1 ppm. (5,6). Since then (5,6), the Threshold Limit has been reduced to 1 ppb.

Cylinder Storage

Upon receipt, the pressure in each carbonyl cylinder was checked, and where necessary, nitrogen was added to 5 psig. to guard against in-leakage which could result in an explosion. After the outlet had been capped to guard against leaky valves, the cylinders were stored outside the laboratory building on an isolated cylinder pad. Shade screens were provided to protect the cylinders from the sun's rays. Before the screens were used, solar heating caused sufficient thermal decomposition to produce carbon monoxide pressures as high as 100 psig. When high cylinder pressures were encountered, the gases were bled off slowly through a flame arrestor and were then burned. This operation was performed in a hood.

No more than one cylinder was allowed in the laboratory at any time. This cylinder was stored in a hood.

Operating Precautions

All nickel carbonyl operations were performed in hoods with sufficient exhaust capacities to maintain face velocities of at least 150 feet per minute. Leak-tight systems were considered mandatory. No operation was started if carbonyl outleakage could be detected by the hydrogen flame test. Aiken and Box, in this laboratory, have demonstrated that this test is capable of detecting nickel carbonyl at concentrations as low as 1 ppm. To guard against explosion hazards resulting from the inleakage of oxygen, all operations* were performed above atmospheric pressure. Wherever possible, the systems were purged in preference to evacuation. In fact, the evacuation operations were limited to those required in filling the saturator. When it was necessary to remove portions of the apparatus, for instance, the test section, the hydrogen flame test was again employed to determine if the equipment could be handled safely outside the hood.

Chemox masks were stored outside the gas plating room for use in the event of hood failure or a nickel carbonyl release. Arrangements were made to seal the gas plating room from the rest of the laboratory in the event of release, with special attention being paid to the air conditioning system. At the present time, air-hose masks are used routinely in nickel carbonyl work because of the lower threshold limit.

Carbonyl Detection

As a warning against undetected leaks, a hydrogen flame was kept burning in the hood, and a second flame was kept burning in the laboratory room.

Carbonyl Disposal

The disposal of nickel carbonyl was held to a minimum. As an example, the carbonyl collected in the mist separators was eventually vapor-transferred back to the saturator. When it became necessary to dispose of the nickel carbonyl, it was vaporized at low concentrations, usually less than 5% in a stream of hydrogen. The hydrogen was then burned in a hood, and the combustion products were taken off through the hood vent.

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* Small amounts, $< 1\%$, of oxygen were deliberately added to the carbonyl containing carrier gas in some experiments. While there was no evidence of reaction in the flowing gas stream, every effort was made to exclude oxygen from closed systems, since explosions have occurred under these conditions.

Precautions were also taken in disposing of piping or equipment used in the gas plating studies. The first step was to purge this equipment, passing the purge gases through a flame or decomposition tube. During purging, the equipment was heated, using a torch where necessary. The equipment was then removed from the system, capped, and melted or buried. Special care was also taken with vacuum pump oil. When oil changes were made, the used oil which contained some nickel carbonyl was burned in an isolated area.

RESULTS AND DISCUSSION

EFFECT OF CATALYSTS ON PLATING RATES AT ELEVATED TEMPERATURES

The results of 15 catalytic gas plating tests on 6-inch sections of 1/2-inch iron pipe are presented in table II. The runs were all made with a system pressure of 2 psig., using carbon dioxide as the carrier gas. The carrier gas flow rate was held constant at 1.4 l./min. in all tests. For 20% nickel carbonyl in the carrier gas, this flow rate at 2 psig. and 100°C. is equivalent to a Reynolds number of 380 in the 1/2-inch pipe. While most nickel carbonyl gas plating work is done using turbulent flow, a Reynolds number of 380 is high enough in the laminar region to avoid powder formation in the gas stream and is also high enough to provide adequate contact between the nickel carbonyl and the pipe wall.

The results of the plating studies are shown graphically in figure 5, where the logarithm of the plating rate is plotted as a function of the reciprocal of the plating temperature. For the control runs, tests 2 and 6, as well as the runs with the hydrogen sulfide catalyst, test 3, 4, and 15, and the runs with the hydrogen sulfide-water vapor catalytic mixture, tests 7, 9, 11, 13, and 14, lines have been drawn through the data points. More data would be needed to determine if the difference in the slope of the lines for the three different plating mixtures is real.

Plating rates obtained with the various catalysts at 100°C. are compared with the results obtained without catalysts in table III. A 25% reduction in plating rate was observed when water vapor was present in the plating mixture at the 0.16% level. A similar reduction in rate occurred when 1.3% ammonia was added; however, the decreased plating rate in this test may have been caused by the lower average nickel carbonyl concentration, 6.8%. With 0.43% hydrogen sulfide, an increase in plating rate of 54% was obtained.

TABLE II

CATALYTIC GAS PLATING TESTS

			Gas Concentration, %						
Run Number	Temperature, °C.	Time, min.	Nickel Carbonyl	Ammonia	Hydrogen Sulfide	Water Vapor	Oxygen	Plate Thickness, mil	Plating Rate, mil/hr.
1	100	60	6.8*	1.3				0.50	0.50
2	100	60	18.8					0.68	0.68
3	100	40	24.2		0.43			0.70	1.05
4	120	50	23.3		0.43			1.70	2.04
5	100	31	21.0		0.78		1.04	2.00	3.90
6**	180	27	24.7					3.50	7.80
	100	5	24.7		0.78				
7	100	60	25.2		0.78	0.03		2.40	2.40
8	100	30	23.1		0.80		0.80	1.50	3.00
9	100	60	20.6		0.73	0.03		2.50	2.50
10	100	60	21.6			0.16		0.50	0.50
11	150	30	21.1		0.54	0.08		7.00	14.00
12	180	20	21.8					8.00	16.00
	145	10	21.1		0.54	0.08			
13	100	60	21.7		0.32	0.08		3.00	3.00
14	120	60	18.3		0.22	0.08		3.75	3.75
15	120	60	21.8		0.17			3.75	3.75

* The saturator ran dry during this test.

** Virtually all plating occurred in the first part of the run, i.e., without catalyst.

Note: All tests were run with a carbon dioxide carrier gas flow of 1.4 l./min., i.e., a Reynolds number of 380, and a system pressure of 2 psig.

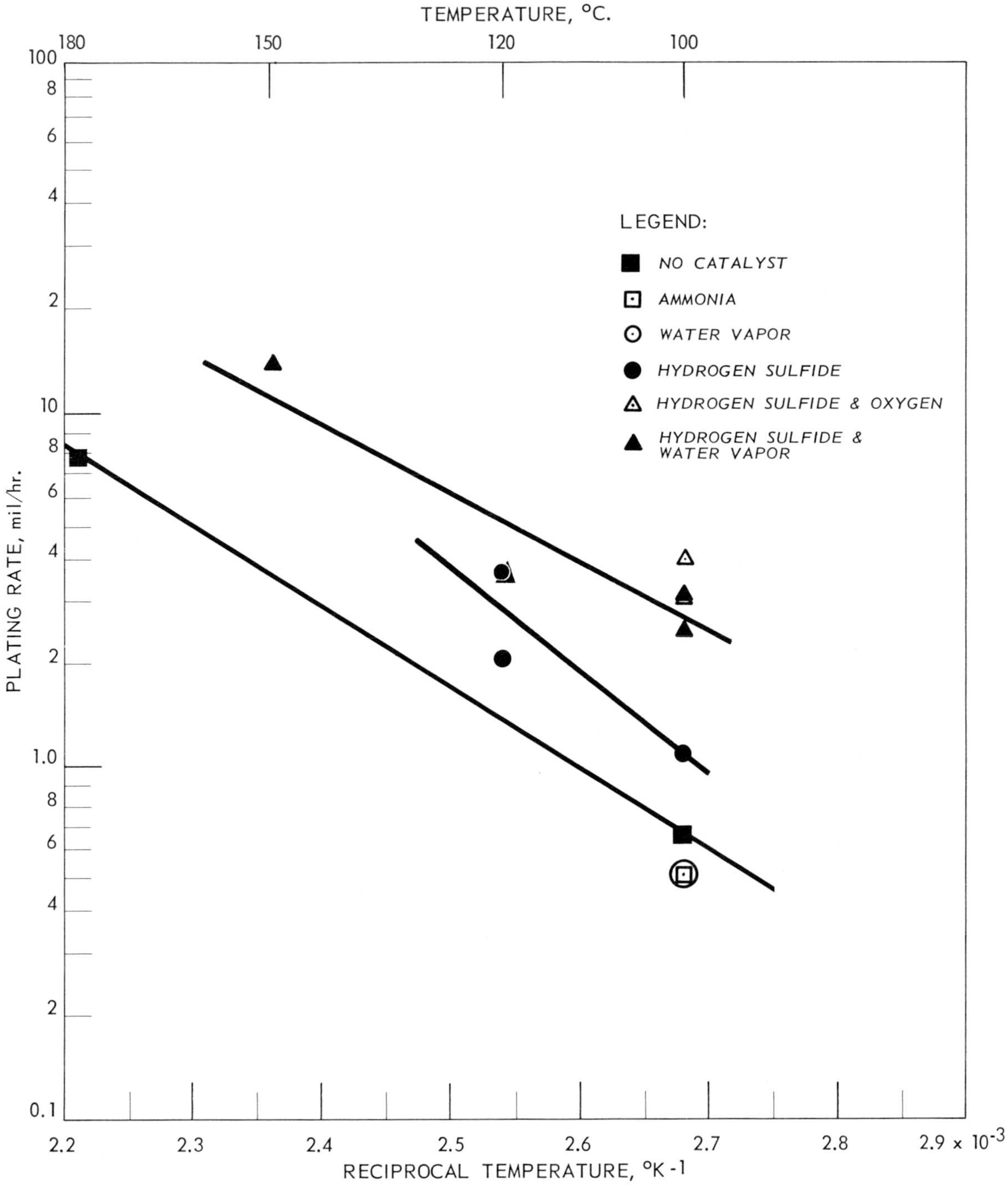

Figure 5
CATALYTIC PLATING RATES

TABLE III

EFFECT OF CATALYSTS ON PLATING RATE

Catalyst	Plating Rate at 100°C. Absolute Rate, mil/hr.	Relative Rate	Equivalent* Plating Temperature, °C.
Water Vapor	0.50	0.73	90
Ammonia	0.50	0.73	90
None	0.68	1.00	100
Hydrogen Sulfide	1.05	1.54	114
Hydrogen Sulfide-Water Vapor	2.62	3.85	141
Hydrogen Sulfide-Oxygen	3.45	5.07	150

* The equivalent temperature is the temperature needed for plating with nickel carbonyl, i.e., no catalyst, to achieve the plating rate observed for nickel carbonyl plus catalyst at 100°C., using the curves in figure 5.

Using mixtures of hydrogen sulfide and water vapor containing 0.32 to 0.78% hydrogen sulfide and 0.03 to 0.08% water vapor, an almost fourfold increase in plating rates was achieved, while the rate was increased by a factor of 5 through the use of mixtures of hydrogen sulfide and oxygen, containing 0.78 to 0.80% hydrogen sulfide and 0.80 to 1.04% oxygen.

The catalytic effect can be used to reduce the plating temperature instead of increasing the plating rate. This is shown in terms of equivalent plating temperatures in table III. The equivalent plating temperature is defined as the temperature required with nickel carbonyl to produce the plating rate which can be obtained with nickel carbonyl and the catalyst at 100°C. For nickel carbonyl without catalyst, a plating temperature of 150°C. would be required to obtain the plating rate achieved using the hydrogen sulfide-oxygen catalytic mixture at 100°C.

Except for run 1, where the average nickel carbonyl concentration dropped to 6.8% when the saturator ceased bubbling, there is no evidence that variation in carbonyl concentration between 18 and 25% had any significant effect on the plating rate. For instance, the operating conditions in tests 7 and 9 were essentially the same except for the carbonyl concentrations which were 25.2 and 20.6%, respectively. The agreement between the plating rates in these two runs, 2.4 and 2.5 mils/hr., respectively, was well within the experimental error.

There are some indications of a concentration effect for the hydrogen sulfide catalyst, with higher plating rates at a lower concentration. In test 4, where the hydrogen sulfide concentration was 0.43%, the plating rate was 2.0 mils/hr. The operating conditions for test 15 were the same as for test 4, except for the hydrogen sulfide concentration which was 0.17%, and the plating rate in this run was 3.8 mils/hr. More tests are needed to confirm this observation.

Preliminary tests were made to assure that the oxygen or water vapor concentrations were high enough to produce a significant catalytic effect when mixed with hydrogen sulfide. This was done by impinging a jet of the plating gas on a piece of cardboard at room temperature. If the concentration was too low, plating would start around the outer edge where oxygen from the atmosphere mixed with the jet, frequently leaving an unplated spot in the center of the card. This procedure merely assured that there was sufficient oxygen-containing material present to have a significant catalytic effect. The concentration was not optimized.

There are some indications that the plating rate increased with increasing concentrations of water vapor in the hydrogen sulfide-water vapor mixture or oxygen in the hydrogen sulfide-oxygen mixture. For instance, all other conditions were essentially constant in tests 5 and 8, but the oxygen concentrations were 1.04 and 0.80%, respectively, and the plating rates were 3.9 and 3.0 mils/hr., respectively. In tests 7 and 9 at 100°C., the hydrogen sulfide concentrations were 0.78 and 0.73, respectively, and the water vapor concentration was 0.03%. The average plating rate for these runs was 2.5 mils/hr. In run 13 at 100°C., with 0.32% hydrogen sulfide and 0.08% water vapor, the plating rate was 3.0 mils/hr. Again, more data are needed.

PROPERTIES OF THE NICKEL PLATE

The conventional nickel carbonyl gas plating process produces a ductile, high purity nickel plate which is dull gray in color. By maintaining adequate flow velocity of the plating gas over the work, nickel powder inclusions can be avoided. The bond between the plate and the substrate is almost always reported as mechanical; however, heat treatment can be used to produce diffusion bonding.

The properties of the bond depend on the condition of the surface of the article being plated. A dirty, greasy, or rusty surface will cause poor mechanical bonding. Moreover, the presence of foreign material or a thick oxide layer between the base metal and the plate will make it impossible to develop an effective diffusion bond. Similarly, poor mechanical adherence between the plate and the pipe surface can result in poor diffusion bonding.

The cleaning procedure used on all test sections was developed in connection with conventional nickel carbonyl gas plating operations, using temperatures in the 140 to 180°C. range. This procedure produced a clean pipe surface with a thin oxide layer and resulted in good mechanical bonding between the plate and the pipe. Some additional improvement in bonding was achieved either by outgassing the test sample for 1 hour at 300°C. or by reducing the sample with hydrogen for 1 hour at 300°C.; however, the improvements were considered too small to justify reduction or outgassing in the catalytic plating studies.

The use of the hydrogen sulfide catalyst, either alone or in combination with water vapor or oxygen, had a significant effect on the characteristics of the plate. In general, the plate had a smooth, shiny surface but was brittle. Where sections of pipe plated by the conventional process could be subjected to a reverse bend test without damaging the plate, the same treatment would produce cracks in the plate formed with the catalysts. In extreme cases, the plate would shatter and pull loose from the substrate. The addition of water vapor or ammonia to the carbonyl-carrier gas mixture resulted in plates with the same properties as those produced by the conventional process.

The results of microscopic examination of the nickel plates are presented in table IV. Some treeing was evident for run 2, where no catalyst was used, and for run 10, where water vapor which had no catalytic effect was added to the plating gas. Rough surfaces were observed for run 1 where ammonia addition did not increase the plating rate.

In other runs where the hydrogen sulfide catalyst was used, either alone or mixed with water vapor or oxygen, the plate was characterized by smooth surfaces, high density with occasional cracks or porosity which normally did not penetrate through the plate, and occasional inclusions of a crystalline material which may have been nickel sulfide. Typical examples of the cracks, porosity, and crystalline inclusions are shown in the photomicrographs in figures 6 and 7.

For runs where hydrogen sulfide was employed, there was no clear cut correlation between plating variables such as temperature or concentration and the characteristics of the plate such as surface roughness, porosity, or inclusions. The adherence of the plate also appears to have been independent of plating conditions. In fact, adherence improved with run number, suggesting that the good mechanical bonding in later runs may have resulted from a general improvement in technique.

In runs 6 and 12, a two-step plating operation was employed. First, a ductile, nonporous nickel layer was deposited by the conventional plating process. Next, an attempt was made to produce a smooth, shiny plate using the catalytic process. The attempt in run 6 was unsuccessful. Too little nickel was deposited under catalytic conditions to affect the surface condition of the plate which was typical of those formed without catalysts. The second-step catalytic surfacing operation was more

TABLE IV

EXAMINATION OF NICKEL PLATE

Run Number	Temperature, °C.	Catalysts	Microscopic Examination	Corrosion Test Results
1	100	NH_3	Rough surface, shattered, no adherence.	No rust
2	100	None	Some treeing, poor adherence.	No rust
3	100	H_2S	Shattered, inclusions and porosity, poor adherence.	Many rust spots
4	120	H_2S	Smooth surface, porosity and inclusions, poor adherence.	No rust
5	100	H_2S, O_2	Smooth surface, few cracks, and some porosity.	One small rust spot
6	180 100	None H_2S	Moderately smooth surface, dense, no evidence of second layer.	No rust
7	100	H_2S, H_2O	Smooth surface, dense, uniform, good adherence.	Rust along crack in plate
8	100	H_2S, O_2	Smooth surface, shattered, no adherence.	Three small rust spots
9	100	H_2S, H_2O	Smooth surface, dense, occasional crack, good adherence.	
10	100	H_2O	Some treeing, nonporous, good adherence.	
11	150	H_2S, H_2O	Smooth surface, nonporous, good adherence.	
12	180 145	None H_2S, H_2O	Smooth surface, nonporous, good adherence.	
13	100	H_2S, H_2O	Smooth surface, nonporous, crystalline inclusion, good adherence.	
14	120	H_2S, H_2O	Smooth surface, nonporous, good adherence.	

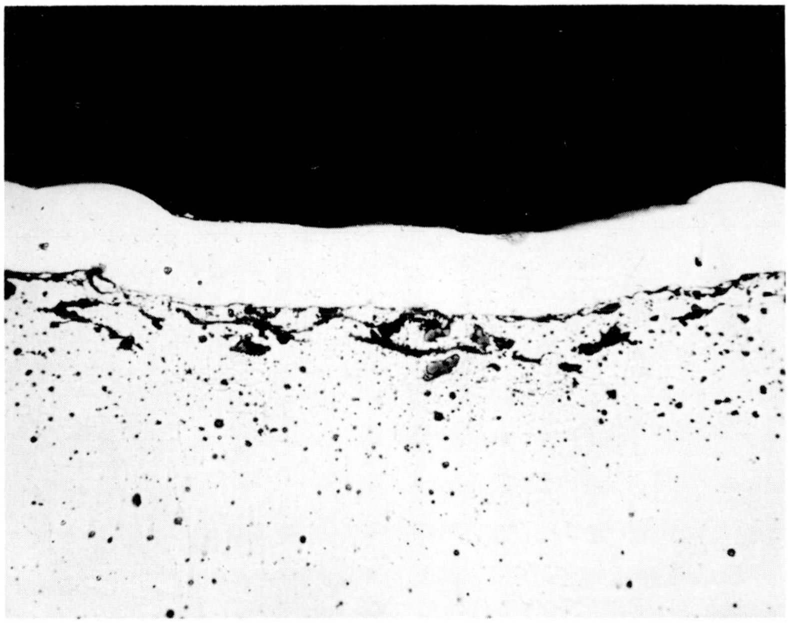

Figure 6

TYPICAL CATALYTIC PLATE, HYDROGEN SULFIDE CATALYST, 500X MAGNIFICATION

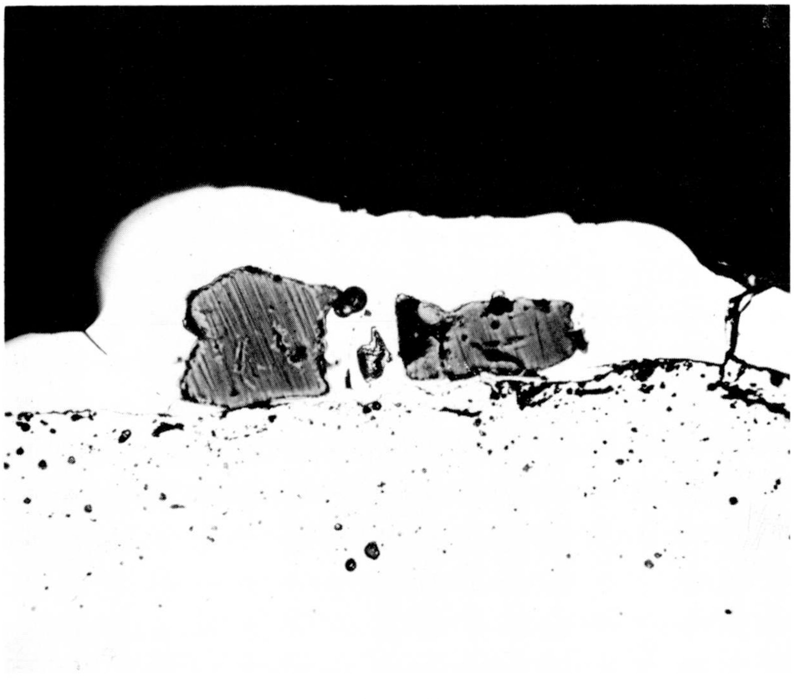

Figure 7

CATALYTIC PLATE SHOWING INCLUSIONS, HYDROGEN SULFIDE CATALYST, 500X MAGNIFICATION effective in run 14 where a higher temperature and a longer plating time were employed. The plated surface was smooth and shiny, and no demarkation between the conventional plate and the catalytic plate could be detected by microscopic examination at 500 X. This is not unexpected, as the sample was not exposed to the atmosphere between the two plating runs.

The results of corrosion tests are also presented in table IV. In many cases, no rust was observed. When the corrosion test resulted in rust spots, they appeared to be associated with isolated imperfections in the plate except for run 3, where the plate was thin and porous. Again, except for run 3, there was no obvious relationship between corrosion test results, plating conditions, and the appearance of the plate as determined by microscopic examination.

A sample of the plate from run 9 was stripped loose from the pipe and subjected to chemical analysis. The analyses showed 0.62% sulfur, 0.17% oxygen, and 0.002% carbon. The results indicate that some of the hydrogen sulfide was combined in the nickel plate, probably as nickel sulfide and possibly as crystalline nickel sulfide inclusions. The sulfur concentration in the plate was equivalent to 32% of the hydrogen sulfide used as catalyst. The high oxygen content is unexplained, as all the oxygen present in the water vapor catalyst would only be equivalent to 0.04% oxygen in the plate. Perhaps, it was caused by oxidation which occurred after plating. The low carbon concentration is typical of results obtained with conventional gas plating at low temperatures.

Samples of pipe plated by either the conventional or the catalytic process were heat-treated in hydrogen for 1 hour at 600 and 800°C. Upon microscopic examination, it was evident that diffusion bonding to a depth of about 0.1 mil had occurred on both samples heated to 800°C. There was no alloying on the samples heat-treated at 600°C. Sections of both samples heat-treated at 800°C. were subjected to a reverse bend test without apparent damage to the plate.

In summary, it should be emphasized that a brief scoping study was performed on catalytic gas plating. There is need for additional work on the effect of catalyst concentrations and also on the characterization of the nickel plate. It would be desirable to investigate further the two-step plating process to determine whether it is possible to produce plates combining the ductility of the conventional plate with the smooth surface of the catalytic plate.

GAS PLATING AT ROOM TEMPERATURE

A series of exploratory experiments was performed to investigate the possibility of catalytic plating with nickel carbonyl at room temperature. For these special studies, a vertical glass tube was connected to the gas plating system at the location shown in figure 1. The glass tube was enshrouded in a glass funnel, as shown in figure 8, to shield the jet of plating gas from the air. A glass shield was placed in front of spray-jet to divert unreacted nickel carbonyl away from the experimenter toward the back of the hood. The hydrogen flame test failed to reveal nickel carbonyl in the area where the experimenter was working; however, if these experiments were repeated today, air-hose masks would be used and other personnel would be excluded from the room. Adequate dilution is needed in the hood exhaust to avoid contamination of surrounding areas.

Most of the experiments were performed by holding a 3-inch by 5-inch file card, one centimeter below the outlet of the glass tube. In every test, the carbon dioxide carrier gas contained approximately 20% nickel carbonyl. The flow rate of the carbon dioxide was varied from 0.6 to 1.4 l./min. without apparent effect on the results.

When no catalyst was employed, no plating occurred in 100 seconds. With hydrogen sulfide catalysts present in the 0.4 to 0.7% range, plating was evident in 5 to 10 seconds; however, it always started at the edge of the card, suggesting that oxygen which diffused from the surrounding atmosphere was also a catalyst. Next, both hydrogen sulfide and oxygen were used to catalyze the plating reaction. Plating did not start at the point where the jet impinged on the card until the oxygen concentration was above 10%. Ammonia seemed to catalyze the reaction, forming a black, nonconducting deposit. Hydrogen seemed to have a similar effect, producing a black, conducting deposit which formed at the edges of the jet.

With the hydrogen sulfide-oxygen mixture, plates were formed on the cards which are still bright and shiny after 12 years. Microscopic examination of the cards indicated that individual fibers were coated. The film did not deposit on the printed lines, nor did it deposit on spots made damp with water. A dull black deposit was formed on spots dampened with acetone.

Continuing with the hydrogen sulfide-oxygen catalytic mixture, no plate was formed on newsprint, and only a very slight deposit was formed in 100 seconds on a glossy color print from a magazine. The following articles were readily plated: bond paper, cotton cloth, cork, copper, aluminum, and iron. With cloth, paper, and cork, the plate followed the surface of the material; there was no evidence of bridging across pores. In all cases, the bond was good.

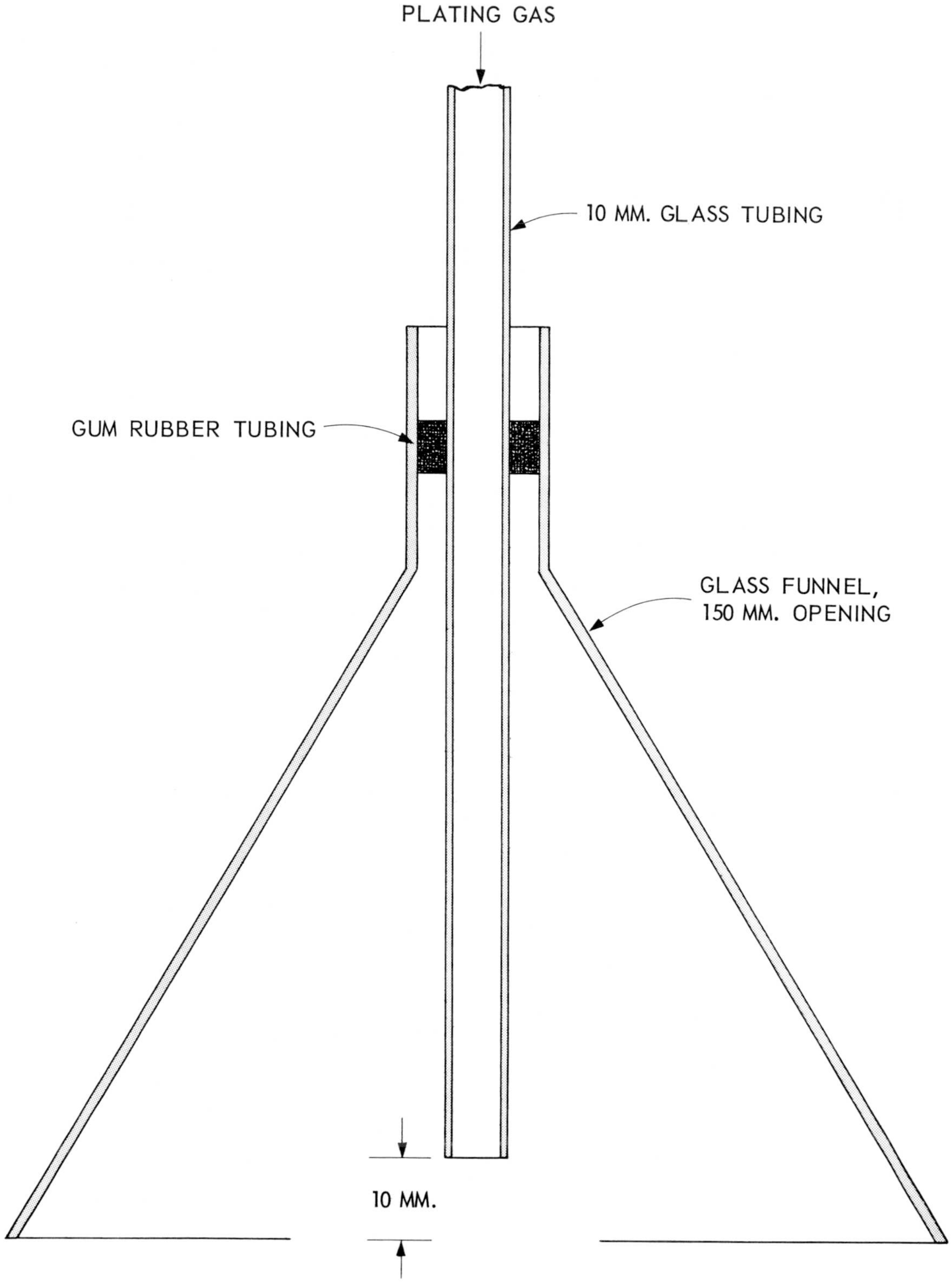

Figure 8
ROOM TEMPERATURE PLATING ATTACHMENT

It was possible to solder to a heavy film deposited on bond paper. After use of hydrochloride acid flux, molten soft solder was dropped on a pretinned electrical lead held in contact with the plate. A strip, one-inch wide and 3-inches long, began to heat when 5 V. ac. potential was applied across it.

Finally, the possibility of depositing transparent films which could be used to heat glass was investigated. A thin film was plated on a glass microscope slide. The center was then covered with another slide placed crosswise, and a thicker film was deposited on the ends where the electrical circuits were to be soldered. Thus, a thin one-inch square plate was prepared. No appreciable heating was observed with 100 V. ac. potential unless the resistance of the film was below 1000 ohms. To reach this resistance level, a dark but not opaque film was needed. When the film was heated enough to boil a drop of water, blistering invariably occurred immediately under the water.

The thickness of films plated on glass, calculated from the specific conductance of nickel and the measured film resistance, was between 1 and 10 A. Since films this thin would not have been visible, it is obvious that the plates must have been discontinuous or porous. Thus, these plates were probably not effective protective coatings.

Nickel deposition rates were not measured for the room temperature plating runs; however, extrapolation of the results obtained with the hydrogen sulfide-water vapor catalytic mixture indicate that plating rates of about 0.3 mil/hr. could be obtained at room temperature. This is a low rate for the formation of a protective coating by gas plating; however, catalytic room temperature plating may have applications for the deposition of decorative coatings on articles which cannot be subjected to higher temperatures. The room temperature process might also be used to form a conducting surface on nonconductive materials, thus making it possible to electroplate these materials.

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