

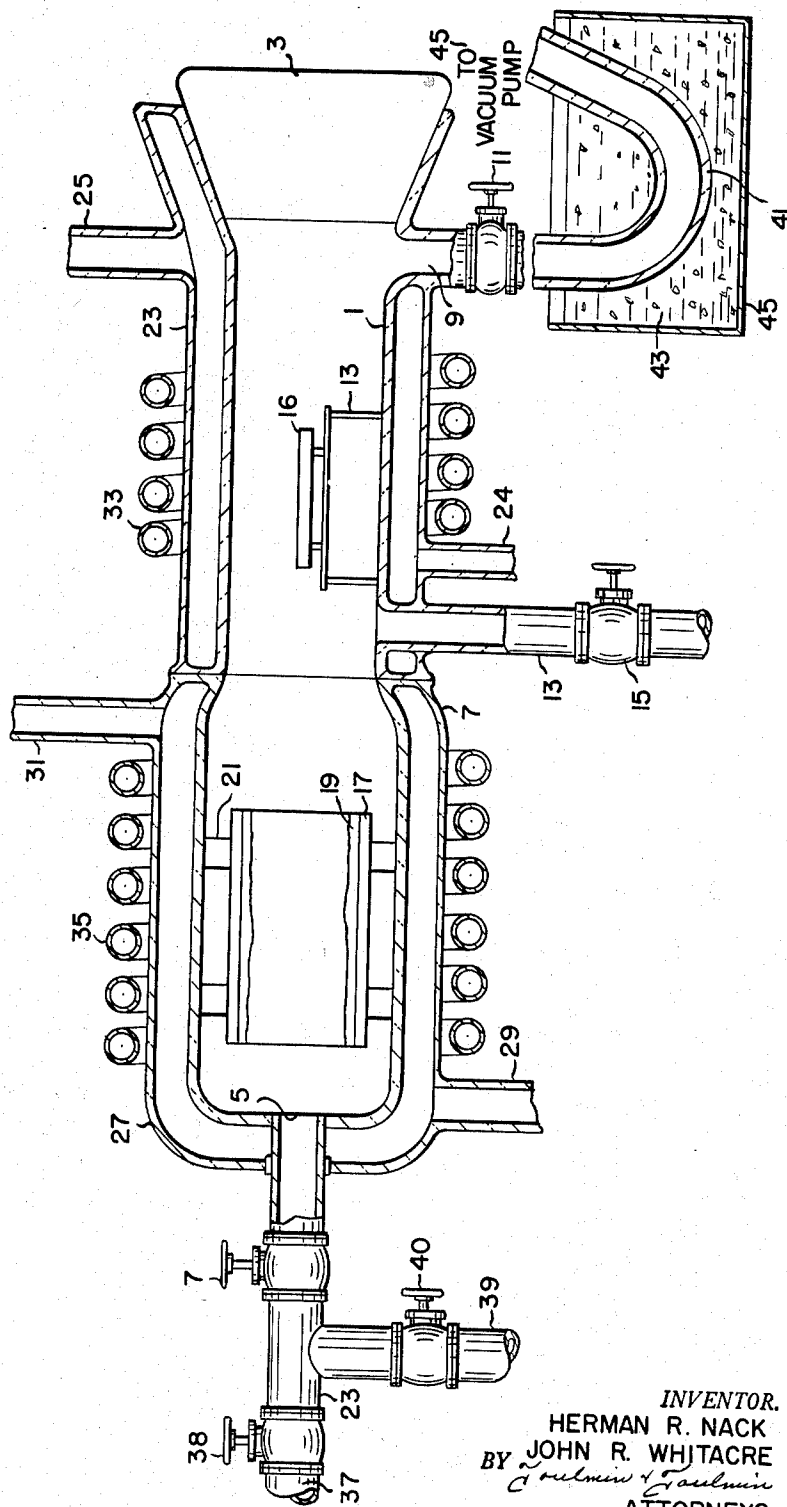
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CATALYZED DEPOSITION OF METALS FROM THE GASEOUS STATE

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CATALYZED DEPOSITION OF METALS FROM THE GASEOUS STATE

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This invention relates to the deposition of metals from the gaseous state. More particularly the invention relates to the deposition of nickel from nickel carbonyls by thermal decomposition.

This application is related to co-pending application of Herman R. Nack, Serial No. 324,963 filed December 9, 1952, and assigned to the same assignee as the present invention.

The deposition of nickel coatings on metals, such as iron and steels, has previously been practiced with varying degrees of success. Adhesion of the coating to the base metal, always a serious problem, has been achieved in a suitable manner for some applications. Efforts in the field have been directed to improving this adhesion in order that a product having a coating firmly bound to the base metal may be attained. These researches have considered the effects of various carrier gases for the carbonyls, the influence of flow rates, temperature, plating pressure, impurities, inter-gaseous decomposition, and so forth. The problem of securing a plate having suitable adherence to a base for all conditions of use however has remained present.

It has now been discovered that the adherence of the plating of nickel deposited from nickel carbonyl onto a base metal, such as iron and hot or cold rolled steels, may be materially improved, to the extent that a long thin sheet of the base when coated with nickel may be doubled upon itself without causing a buckling or separation of the coating from the base in any degree. In other words the coating and base remain completely integral under severe mechanical stress.

It is therefore a primary object of this invention to set forth a novel process for the deposition of nickel from nickel carbonyl.

It is a principal object of this invention to describe a novel treatment of a base metal prior to the introduction of the nickel carbonyl thereto.

It is a further object of this invention to describe a novel treatment of carbon monoxide gas to enhance the properties thereof for treatment of a base metal.

These and other allied objectives of the invention are attained, generally speaking, by utilizing a catalyzed carbon monoxide gas both as a cleansing medium and as a carrier gas for the nickel carbonyl in the plating process.

The carbon monoxide gas in accordance with the precepts of this invention is itself exposed to, that is, is passed over, what may be termed 'active nickel' a process which in some not completely analyzed manner enhances the action of the carbon monoxide. Thus it has been discovered that if a base metal to be plated is heated to a temperature in excess of 500° F. and carbon monoxide which has passed over freshly deposited nickel, is brought into contact with the base metal, the surface thus prepared is very receptive to the metal of the nickel carbonyl upon subsequent plating.

The "active nickel" has been referred to as "freshly prepared"; it is only necessary that the "active" nickel be pure metal—that is—unoxidized. Generally speak-

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ing we have found that a nickel deposit which has been exposed to air over a weekend and consequently oxidized is ineffective to condition the carbon monoxide gas for the attainment of the objectives of this invention.

It is to be noted however that nickel metal which is unoxidized may be utilized repeatedly in the production of plated objects without apparent loss of efficiency. Thus, for example, a gas plating chamber may be fitted with a hollow steel cylinder coated on the exterior with deposited nickel which has not been exposed to the atmosphere and the nickel contents of this tube will serve indefinitely to catalyze the action of the carbon monoxide gas passing therethrough.

The method of securing the nickel deposit is not critical but deposition from the gaseous state is considered advantageous and as will hereinafter be described the nickel will be continually rejuvenated by the practice of the noted processes.

In the process of invention the nickel over which the carbon monoxide passes should be at a relatively high temperature, that is, above 1200° F. Nickel has a tendency to assist the decomposition of carbon monoxide into carbon dioxide and at low temperatures the equilibrium tends to favor production of the latter with carbon formation which of course is undesirable. Maintaining the temperature high favors the carbon monoxide.

It is to be noted also that carbon monoxide at temperatures below 1525° F. is a strong reducing agent, stronger for example than hydrogen and it is accordingly desirable to maintain the carbon monoxide temperature below this limit.

Accordingly while the process described hereinafter is operable over a wide range it is highly desirable that the carbon monoxide gas be maintained within the temperature limits of 1200° F. to 1525° F. While carbon dioxide is formed more easily at the lower temperatures its presence to some extent can be tolerated due to the highly effective reducing action of the carbon monoxide present at the lower temperatures. Since however carbon may deposit on the nickel when carbon dioxide is formed adherence to the stated temperature range for the nickel and carbon monoxide gas is recommended.

An important feature of the present invention is that the object to be plated need not be raised to unduly high temperatures to effect either the cleaning or the plating operation; thus with gun barrels it is generally desirable when plating the interior that the barrel itself be maintained at 750° F. or less. With the present invention the carbon monoxide gas passed over the active nickel may suitably and preferably be heated to much higher temperatures as 1200° F. to 1500° F., and then brought in contact with the surface to be plated to effect cleaning of the same; the body of the barrel may be at a much lesser temperature, that is 500° F. and the slowly flowing stream of hot carbon monoxide will not affect the body detrimentally. The resultant effect however is the attainment of a surface eminently suitable for the receipt of the nickel coat.

Accordingly the process of invention involves the separate heating of a workpiece and active nickel to temperatures above the normal plating range for nickel carbonyl and the passing of the carbon monoxide gas to the nickel and workpiece successively. Thereafter the temperature of the workpiece is permitted to drop to that of the normal plating range for nickel carbonyl and the temperature of the nickel is permitted to fall below the plating range—this is to about 100° F. or less.

While the temperatures of these members are falling a very slow flow of carbon monoxide and nickel carbonyl is fed over the nickel to the workpiece. This flow should be initiated while both the nickel and workpiece are above normal plating temperature. While under this

circumstance some decomposition of the carbonyl may take place on the nickel, this will merely serve to keep the nickel rejuvenated. The carbonyl which passes the nickel will deposit on the workpiece as a thin adherent film. This step is apparently necessary to obtain optimum adhesion as coatings obtained when the initial flow is made at lower temperatures are not as tenacious.

However the temperature of the nickel should be below the decomposition point of the nickel carbonyl prior to the introduction of heavy carbonyl flow to avoid excessive premature decomposition.

The deposit of nickel over the adherent preliminary coat takes place uniformly and the nickel adheres tenaciously, the thickness of the coat within normal limits having little or no effect upon the adhesion; this has been illustrated by preparing a thin sheet of hot rolled steel in accordance with the precepts of the invention and subjecting the sheet to a severe bending—sufficient to rupture the metal of the sheet—there was no apparent separation of the nickel from the base even at the rupture and the nickel could not be worked loose by prying at the same at the point of rupture. Such sample test pieces involve coatings of 3–5 mils on a strip .010" thick. Many processes for nickel deposition have been devised and investigated but no coating save that prepared in accordance with co-pending application of Herman R. Nack, filed of even date herewith, has withstood this rigorous test. In fact so far as is known no other gas plating method has provided a bond which is at all analogous.

The invention will be more fully understood by reference to the following detailed description and accompanying drawing wherein the single figure of the drawing is a schematic view illustrating a complete apparatus useful in the preferred embodiment of the invention.

Referring to the drawing there is shown at 1 a glass vessel having a removable stopper 3, an inlet 5 controlled by valve 7 and an outlet 9 controlled by valve 11. Auxiliary gas inlet 13 is controlled by valve 15 and is provided as a bypass to permit the introduction of carbon monoxide borne nickel carbonyl gas.

Positioned in vessel at the right hand side is a small platform on which may be mounted the base metal, in this case a cold rolled steel sheet 16. Positioned at the left hand end of the vessel is a tubular member 17 coated internally with active nickel 19, the tube being supported in the vessel in any suitable manner as by member 21.

A first water jacket 23 surrounds the right hand end of the tube and is suitably provided with inlet 24 and outlet 25. A second water jacket 27 having inlet 29 and outlet 31 abuts jacket 23 from the left and surrounds vessel 1 adjacent the member 17. Separate water jackets are preferable to enable rapid cooling of the member 17 from the high temperatures employed; however a single jacket will serve, it being then only necessary to control the input to the induction heat coil 33 to maintain the workpiece 16 at proper temperature. For similar reasons of control a separate induction heating coil 35 surrounds the left hand end of vessel 1.

A conduit 37 is valved at 38 for the passage of carbon monoxide and is indicated at the left hand end of the figure as is a conduit 39 having valve 40 for the passage of nickel carbonyl. In practice it is generally desirable to vaporize the normally liquid nickel carbonyl (B. P. 44° C.) with a flow of warmed carbon monoxide but any suitable method of vaporizing the carbonyl may be employed.

At the right hand end of the vessel 1 outlet 9 terminated in a U-shaped portion 41 surrounded by Dry Ice or other cooling medium 43 contained in tank 45. The outlet of portion 41 is connected to a vacuum pump 45 adapted to hasten the removal of gases from vessel 1.

Prior to positioning cold rolled steel workpiece 16 the same is cleaned preferably by abrasion and a trichloro-

ethylene treatment and the dried and cleaned object is then inserted in vessel 1 and stopper 3 inserted.

Then with valve 7 closed, valve 11 open, vacuum pump 45 operating and coils 33 and 35 supplying heat to the vessel, the same is evacuated. While such precautions are not always necessary and the air of the vessel may be forced out by the subsequent carbon monoxide flow it is believed that evacuation is desirable in the manner described in order to consistently attain optimum results.

The temperature of member 17 is then raised to approximately 1300° F.–1350° F. and the temperature of workpiece 16 to about 650° F. by means of induction heating coils 35 and 33 respectively; thereafter valves 7 and 38 are opened to permit a flow of carbon monoxide from any suitable source such as a tank of commerce or in some instances a re-cycling operation from other processes. The monoxide flow is relatively slow, preferably about 0.1 liter per minute.

The flowing monoxide thus in its passage through the nickel attains a high temperature and exerts in its contact with the workpiece 16 a strong reducing action, apparently greater than that occasioned by hydrogen under similar conditions. The nickel also tends to increase the activity of the gas for less effective results judged by adhesion characteristics of the product, are attained if merely heated gas under the same conditions is passed to the workpiece.

Under the stated conditions a time of about 10 minutes is sufficient to insure of the required activation of the cold rolled steel surface (16); the heating is then either reduced or terminated and the temperature of the workpiece is allowed to fall into the normal plating range for nickel carbonyl, that is about 250° F.–450° F. The temperature of the cylinder 17 is at the same time permitted to drop to about 100° F. that is, below the decomposition point of the carbonyl.

However, during these temperature decents nickel carbonyl, preferably carbon monoxide borne in a concentration of about 35% carbonyl, is introduced into the vessel through valve 40; if the carbonyl is heat vaporized carbon monoxide is introduced through valve 38 to mix with the carbonyl in about the same concentration. The flow rate, measured as are all other volumes at room temperature that is 76° F. and atmospheric pressure, is very low—about 10–20 cc. per minute. The initial flow of this gas mixture may occur while high temperatures still exist and the results of testing indicate that for optimum plating the flow must occur while the temperature of the workpiece is still above 500° F. While some decomposition of nickel may occur at cylinder 17 this is not detrimental since it serves by depositing nickel to rejuvenate the nickel content of the cylinder. Sufficient carbonyl as such will pass to deposit a tightly adherent film on the base metal at 16.

Thereafter and while the workpiece temperature is at 250–450° F. the flow of the carbonyl-carbon monoxide mixture at about the same concentration is increased to about 1 liter per minute. The carbonyl then decomposes at the workpiece under the influence of the heat thereof and any desired thickness of nickel may be obtained. Thus in about 20 minutes a deposit of 3 mils is procured with the foregoing procedure. The nickel deposit thus attained is firmly adherent and takes a high polish.

The above procedure may be varied by passing the plating flow, that is, the larger gas flow through auxiliary inlet 13 and valve 15 rather than inlet 5. With this procedure it is then not necessary to drop the temperature of the nickel containing cylinder all the way down to 100° F. in each cycle and production is thus speeded. The exact temperature reduction necessary then will of course depend upon the physical arrangement of the apparatus, but since the vacuum pump will normally be operating there will be little tendency for the plating gas to be drawn towards the cylinder 17.

The following examples illustrate suitable conditions for the practice of the invention:

Example I

Workpiece (base metal).....	Hot rolled steel strip
Preliminary cleaning.....	Abrasion plus acid and alcohol
Heat up time.....	10 minutes
Workpiece temperature attained.....	800° F.
Cylinder temperature attained.....	1250° F.
Carbon monoxide flow.....	10 min. at 1/10 liters per min.
Workpiece temperature (during carbon monoxide flow).....	825° F.-880° F. (Range over 3 points on piece).
Cylinder temperature (during carbon monoxide flow).....	1250° F. (maximum)
Cool workpiece to temperature of.....	330° F.-350° F.
Cool cylinder to temperature of.....	Less than 100° F.
Carbon monoxide and nickel carbonyl (35%) while cooling.....	10-15 cc. per min. for 10 min.
Workpiece temperature.....	850° F.-350° F.
Cylinder temperature.....	1200° F.-100° F.
Cool cylinder to lower than plating temperature.....	Maximum 100° F.
Maintain workpiece at.....	330° F.-350° F.
Carbon monoxide and Nickel carbonyl (35%).....	1 liter per min.

Example II

Workpiece (base metal).....	Cold rolled steel strip
Preliminary cleaning.....	Abrasion plus degreasing in hot trichloroethylene treatment
Heat up time.....	10 minutes
Workpiece temperature attained.....	675° F. maximum
Cylinder temperature attained.....	1,450° F.
Carbon monoxide flow.....	10 min. at 1/10 liters per min.
Workpiece temperature (during carbon monoxide flow).....	630° F.-685° F. (Range over 3 points on piece)
Cylinder temperature (during carbon monoxide flow).....	1,450° F. (maximum)
Cool workpiece to temperature of.....	330° F.-350° F.
Cool cylinder to temperature of.....	Less than 100° F.
Carbon monoxide and nickel carbonyl (35%) while cooling.....	10-15 cc. per min. for 10 min.
Workpiece temperature.....	685° F.-340° F.
Cylinder temperature.....	1,450° F.-100° F.
Cool cylinder to lower than plating temperature.....	Maximum 100° F.
Maintain workpiece at.....	330° F.-350° F.
Carbon monoxide and nickel carbonyl (35%).....	1 liter per min.

In connection with the foregoing it is to be noted that preferable practice for the attainment of optimum adhesion includes the contact of the activated metal base surface with the initial carbonyl gas flow while the base is above the normal plating range of 250° F.-450° F. for the nickel carbonyl. Apparently such contact insures that completely repetitive results will always be attained as far as adhesion is concerned. On the other hand in one instance where the carbonyl was not passed to the workpiece until the same was at a temperature in the lower end of the plating range the coating was not up to the usual standard.

It is also to be noted with regard to the specific data on cylinder and workpiece temperature that such measurements were made by thermo-couples the leads of which pass through the chamber walls; the slight variations in maximum temperature between the workpiece and cylinder where the same are on contact are occasioned by the contour of the coil with respect to these elements. As readings were taken at 3 points on each of the surfaces the figures set out are considered to be completely representative of actual conditions.

It will be understood that the particular physical shape of the active nickel is not critical and that the active nickel may be conveniently positioned on a screen, mesh, on balls of a material capable of withstanding the temperatures involved or may itself be in the form of a wire, in fact any suitable means of retaining the nickel for exposing to gas may be adequately employed for the application of invention.

It will be understood that this invention is susceptible to modification in order to adapt it to different usages and conditions and accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

We claim:

1. A process of gas plating a metal body with nickel from nickel carbonyl, said process comprising introducing said metal body to be gas plated in an enclosure along with nickel metal, heating said metal body to a temperature between about 500 and 800° F. and below the softening point of the metal, heating said nickel metal to a temperature between about 1200-1525° F., passing a stream of carbon monoxide over said nickel metal and metal body while thus heated, and subsequently decreasing the temperature of said nickel metal and said metal body, and thereafter contacting the metal body at said decreased temperature with carbon monoxide mixed with nickel carbonyl to cause decomposition of said nickel carbonyl and deposition of nickel onto the surface of said metal body.
2. A process of gas plating a metal body with nickel from nickel carbonyl, said process comprising introducing said metal body to be gas plated in an enclosure along with nickel metal, heating said metal body to a temperature above the decomposition temperature of nickel carbonyl, heating said nickel metal to a temperature above about 1200° F., flowing a stream of carbon monoxide over said heated nickel metal and over said heated metal body, and then substantially decreasing the temperature of the nickel metal and the metal body being plated, the temperature of said metal body being between about 250°-450° F., and contacting said heated metal body with nickel carbonyl to cause decomposition of said nickel carbonyl and deposition of nickel onto the surface of said metal body.
3. A process of gas plating a metal body with nickel from nickel carbonyl, said process comprising introducing said metal body to be gas plated in an enclosure along with nickel metal, heating said metal body to a temperature of about 800° F. and below the softening point of the metal, heating said nickel metal to a temperature between about 1200-1525° F., flowing a stream of carbon monoxide over said heated nickel metal and over said heated metal body, and decreasing the temperature of the nickel metal to below the decomposition temperature of nickel carbonyl, simultaneously decreasing the flow of carbon monoxide through said enclosure, said metal body temperature being decreased to within the range in which nickel carbonyl heat decomposes, and then increasing the flow rate of carbon monoxide through said enclosure, and introducing nickel carbonyl therein whereby said metal body is plated with nickel.
4. A process of gas plating a metal body with nickel from nickel carbonyl, said process comprising introducing said metal body to be gas plated in an enclosure along with nickel metal, heating said metal body to a temperature of about 650° F., heating said nickel metal to a temperature between about 1300-1350° F., passing a stream of carbon monoxide over said heated nickel metal and said heated metal body, and decreasing the temperature of said nickel metal below the decomposition temperature of nickel carbonyl, maintaining said metal body heated at a temperature at which nickel carbonyl decomposes, and contacting the thus heated metal body with carbon monoxide mixed with nickel carbonyl to cause decomposition of said nickel carbonyl and deposition of nickel onto the surface of said metal body.
5. In a process of gas plating a metal body with nickel by decomposition of nickel carbonyl the pretreatment step of heating said metal body to be gas plated to a temperature of between substantially above the temperature at which nickel carbonyl decomposes while flowing carbon monoxide in contact therewith, decreasing the flow of carbon monoxide thereover and the temperature of the metal body to approximately 250-450° F., and contacting the resultant heated metal body with nickel

carbonyl to bring about decomposition of the nickel carbonyl and deposition of nickel thereon.

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