United States Patent [19]

Niebylski

[11] 3,882,050

[45] May 6, 1975

[54] **METHOD OF DEPOSITING A NOBLE METAL ON A SURFACE OF A NICKEL SUPPORT**

[75] Inventor: **Leonard R. Niebylski,** Birmingham, Mich.

[73] Assignee: **Ethyl Corporation,** Richmond, Va.

[22] Filed: **July 24, 1973**

[21] Appl. No.: **382,069**

Related U.S. Application Data

[62] Division of Ser. No. 211,730, Dec. 23, 1971, abandoned.

[52] **U.S. Cl.**..... **252/472;** 252/477 R; 423/213.5; 117/130 R

[51] **Int. Cl.** **B01j 11/12;** B01j 11/22

[58] **Field of Search**..... 252/472, 477 R; 423/213.5; 23/288 F; 117/130 R

[56] **References Cited**

UNITED STATES PATENTS

3,110,622	11/1963	Hipp	117/130 R
3,116,165	12/1963	Hipp	117/130 R
3,155,536	11/1964	Freeman et al.	117/130 R
3,328,271	6/1967	Kneif et al.	117/130 R
3,719,739	3/1973	Thompson	252/472

Primary Examiner—Winston A. Douglas
Assistant Examiner—W. J. Shine
Attorney, Agent, or Firm—Donald L. Johnson; Robert A. Linn

[57] **ABSTRACT**

Nickel with a surface deposit of palladium is useful as an exhaust gas catalyst. Palladium may be deposited by contacting nickel with a solution of palladium ions. More than one deposition can be used. If a first deposition is followed by contacting the nickel with strong nitric acid, a second palladium deposition will result in an increased amount of palladium on the nickel surface.

1 Claim, No Drawings

METHOD OF DEPOSITING A NOBLE METAL ON A SURFACE OF A NICKEL SUPPORT

This application is a division of application Ser. No. 211,730, filed Dec. 23, 1971, and now abandoned.

BACKGROUND OF THE INVENTION

In recent years extensive research has been devoted to the alleviation of air pollution in many metropolitan areas. Part of this effort has been directed to methods of reducing the unburned hydrocarbons and carbon monoxide emitted with the exhaust gas of internal combustion engines. Various catalytic converter systems have been proposed to accomplish this purpose. With such systems the exhaust gases are passed through a catalytic bed wherein the noxious materials are converted to an inactive form.

Among the catalysts disclosed in the prior art are the supported nickel catalysts of Gross et al., U.S. Pat. No. 3,370,914. That patent also teaches emission reduction with certain nickel additives in gasoline.

This invention pertains to massive forms of nickel such as nickel wire, grid, turnings, lath, and foams. Such forms of elemental nickel having a noble metal surface deposit are exhaust gas catalysts.

The catalytic reaction of hydrogen with nitric oxide in the presence of oxygen has been studied using a noble supported on alumina; Jones et al., *Environmental Science and Technology*, 5, No. 9, September (1971), page 790 et seq. The catalytic decomposition of nitric oxide by metallic oxides has also been studied; Winter, *Journal of Catalysis*, 22, 158–170 (1971). Application of Monel metal to automotive NO_x emissions control has been reported; Bernstein, Kearby, Raman, Vardi, and Wigg, SAE Paper No. 70014, presented at January 1971 meeting, Detroit, Michigan.

SUMMARY OF THE INVENTION

This invention pertains to massive nickel having a surface deposit thereon of a catalytic quantity of a noble metal. Preferably, the noble metal is rhodium, palladium, or platinum, more preferably rhodium or palladium.

This invention also pertains to a method of diminishing the amount of components in exhaust gas, which method comprises contacting engine exhaust with nickel having a noble metal dispersed thereon.

Also, this invention pertains to a method for forming such treated nickel. As an example, this invention pertains to a method of depositing a noble metal on the surface of nickel, said method comprising contacting said nickel with a liquid containing palladium ions in solution until palladium deposition on the nickel surface has substantially ceased, immersing the treated nickel in nitric acid until its surface is activated, and subsequently immersing the treated nickel surface thereby produced in a liquid containing palladium ions in solution, whereby additional palladium is deposited on said nickel.

DESCRIPTION OF PREFERRED EMBODIMENTS

A preferred embodiment of this invention is massive nickel having a surface deposit thereon of a catalytic promoter quantity of a noble metal. Herein, the term "massive nickel" is used to include nickel in a macroscopic object or objects, and is used to exclude (a) the form or forms of nickel impregnated on catalyst supports and (b) the microscopic nickel particles obtainable by decomposition of nickel compounds in a gaseous or liquid medium. By the term as used herein, is denoted nickel objects having sufficient mass of nickel that common physical properties of nickel, e.g., melting point, are discernible. Thus, the term refers to nickel in a solid state where the mass of nickel is such that the common physical properties and surface characteristics, rather than just surface effects, characterize the metal mass.

The nickel metal may be in many forms such as powders, either fine or coarse, turnings, sheet, lath, wires, screens, sintered objects, foams, etc. The foams can be prepared, for example, by using the process of U.S. Pat. Nos. 2,983,597, 2,895,819, 3,300,296, 3,297,431, 2,917,384 or 3,111,396. When foaming by use of a metal hydride or similar foaming agent, the mass to be foamed may be made more viscous by using a viscosity increasing amount of a viscosity increasing agent as per the teachings of Belgian Pat. No. 746,135. Likewise, nickel may be plated or coated on such forms of other metals. In general, such nickel plates will be at least 0.001 inch thick. The nickel may be pure, substantially pure, or an alloy of nickel. In general, the alloy should contain at least about 60 per cent nickel and preferably, at least about 80 per cent by weight. The nickel coats can be mechanically applied by screws or the like, or can be brazed or welded on. Likewise, the plate or coat can be made by hot sintering, coining, dipping, metallizing, pressure cladding, pouring, and burnishing. Likewise, electrophoresis, electrolytic plating, electrochemical plating, vacuum sputtering, vapor plating, and similar process known in the art can be used.

Noble metals which may be used in this invention are rhodium, palladium, iridium, and platinum. Preferably, rhodium, palladium, or platinum is used and more preferably rhodium or palladium.

It is only necessary that a promoter quantity of noble metal be present at the surface of the nickel. How this amount is achieved is not critical. One can use objects made of a nickel-noble metal alloy, if desired. However, such forms are usually expensive and accordingly it is desirable from the economic viewpoint to treat the surface of the nickel, rather than compose the whole object of nickel-noble alloy.

One can deposit noble metal such as palladium by contacting the nickel to be treated with a liquid such as water containing palladium ions in solution.

Usually one prefers to use an aqueous solution having a pH less than 7, because acidic solutions tend to keep palladium ions in solution rather than precipitating. In general, one prefers to use a solution having a pH in the range of about 2.0–6.5 but other acid systems can be used. When necessary, the pH can be adjusted to the desired level with acid such as nitric sulfuric or hydrochloric acid or other acid, either organic or inorganic. The nature or composition of the acid used to adjust the pH is not critical.

One can use any convenient source of noble metal ions, such as a salt of such metals. Nitrates, chlorides, and the like can be used; however, the nature of the anion is not critical.

The concentration of the noble metal salt is not critical. Saturated or more dilute solutions can be used. In general, solutions of concentration of from about 0.5 to about 15 weight per cent are employed. These afford a reasonable deposition rate.

The solution temperature is not critical. Solutions at ambient or higher or lower temperatures can be employed. Mildly elevated temperatures are preferred. In general, good results are achieved using temperatures from about 25° to about 75°C., 48°–52°C. being preferred.

The deposition is not pressure dependent, ambient pressures are conveniently employed; greater or lesser pressures can be used if desired. Ambient atmosphere as well as inert atmospheres such as neon or argon blankets can be used.

It has been noted that the deposition of palladium will cease after a while even when using solutions in which palladium ions were still available for deposition. Although not bound by any theory, it appears the nickel surface becomes inert to deposition or 'passive'.

This state can be overcome by immersing or otherwise contacting the nickel being treated in HNO_3 or other similar oxidizing acid. The nitric acid concentration employed is not critical; but generally is from about 5 volume per cent to about 55 volume per cent, preferably from about 25 volume per cent to about 50 volume per cent; however, greater or lesser amounts can be used. The temperature of the acid can be from about 75° to about 180°F., preferably 90° to 120°F. Hotter or cooler acids can be used for the temperature is not critical. Acids at ambient and mildly elevated temperature are conveniently used.

Other acids can be used. Mixtures of applicable acids can be employed. Thus, one may use mixtures of nitric acid and hydrochloric acid, 1:3 to 1:5. In addition, one may use phosphoric acid, 3 volumes, nitric acid, 1 volume, and sulfuric acid, 1 volume. Still another applicable mixture is nitric acid, 3 volumes, sulfuric acid, 1 volume, orthophosphoric acid, 1 volume, and glacial acetic acid, 5 volumes.

Also, one may return the nickel surface to activity by conducting an electrolytic etch in the presence of either 10 per cent phosphoric acid; 20 per cent perchloric acid in ethanol; 10 per cent perchloric acid and 90 per cent acetic acid; 50 per cent sulfuric acid; acetic acid with 7 per cent water and 5 per cent CrO_3; sulfuric acid, 13–15 weight per cent, plus 56–63 weight per cent orthophosphoric acid, remainder water; sodium chloride, 15 ounces per gallon plus HCl, 0.5 ounce per gallon; or sodium chloride, 7 ounces per gallon plus sodium nitrite, 3 ounces per gallon.

The time of contacting the metal with the acid is not critical; it is only necessary to activate the metal surface. As a general rule, etching away an excessive amount of metal by acid action is not desirable. For the acid concentrations above, contacting times within the range of from about 0.25 minutes to about 5 minutes and preferably from about 0.5 minutes to about 2 minutes are used. Shorter and longer times can be employed if desired.

After acid treatment, recontacting with a solution of noble metal ions of the type and according to the process described above, can be conducted if additional deposition is desired.

The acid treatment can be followed with a water wash or rinse, if desired, but use of such wash or rinse is not critical.

EXAMPLE I

A nickel foam with a 30 (0.030 inch) pore size doped using palladium nitrate. For this, a slightly acid HNO_3 solution was used (10 ml in 250 ml of water). To this was added one gram of $Pd(NO_3)_2$. The salt was difficult to solubilize, therefore, small amounts were added at a time while the solution was warmed (50°–65°C.) and continuously stirred.

The nickel foam was immersed in the solution for 5 minutes. Within a minute the nickel turned color — black grey. After immersion, the foam was dried. Analysis indicated the foam contained 0.07 and 0.09 weight per cent Pd. In a similar manner, rhodium was plated on another sample of nickel foam. The product had 0.2 weight per cent rhodium.

EXAMPLE II

A nickel foam of 30 mil pore size which had been doped with ~ 0.1 weight per cent Pd was treated with 25–30 per cent HNO_3 solution by immersion for approximately 30 seconds and then rinsing in cold running water. This was repeated.

After the acid etch, the foam was redipped in a mixture of 1 gram $Pd(NO_3)_2$, 250 H_2O, and 10 ml conc. HNO_3. The foam was redipped for about 15–20 seconds in the HNO_3 and then dipped in the $Pd(NO_3)_2$-containing solution for a few minutes again.

After drying, the foam was submitted for chemical analysis which indicated 0.32 weight per cent Pd.

EXAMPLE III

Clean nickel turnings, 472 grams, were packed into a 42 cubic inch exhaust emission converter. After packing, the converter with the nickel turnings was dipped in 50 per cent nitric acid, then rinsed with tap water.

A 1,500 ml solution of 1 per cent nitric acid containing 1.0 gram of palladium nitrate was prepared. The catalyst converter with turnings was then immersed in this solution for 15 minutes. After draining and rinsing, the catalyst and converter were dried at 150°C. overnight.

Thereafter, the temperature of the furnace was raised to 540°C. and the converter and catalyst were allowed to stay in this environment for 3 hours.

EXAMPLE IV

After the nickel catalyst of Example III was tested for exhaust gas catalyst activity in accordance with Example VI, the entire converter and turnings were cleaned by immersion in 50 per cent nitric acid. Thereafter, the catalyst containing cartridge was immersed for a half hour in a solution of 2 per cent in nitric acid and containing 10 grams of palladium nitrate. After draining and rinsing in tap water, the catalyst and converter were air dried. Thereafter, the cartridge and catalyst were placed in a furnace at 540°C. and left there overnight.

Two samples of this catalyst were found to contain 0.29 and 0.42 weight per cent palladium.

EXAMPLE V

Roasted nickel turnings, 542 grams, were pressed into a 42 cubic inch capacity converter. The charged converter was rinsed with 50 per cent nitric acid, then rinsed with water and then immersed in a 2 per cent acid solution containing 10 grams of palladium nitrate. The volume of this solution was 1,500 ml and the immersion time was 30 minutes.

After immersion, the cartridge with catalyst was dried at 175°C. for 3 hours in circulating air. It was then placed in a furnace at 540°C. and kept under nitrogen overnight.

Following the procedures of the above examples, catalysts are prepared from nickel turnings, sheet, lath, wires, screens, and foams such that they contain from 0.05 to 1 weight per cent of a metal selected from the class consisting of rhodium, iridium, palladium, or platinum. The foams are produced by the procedures of the above-cited patents, for example U.S. Pat. Nos. 2,983,597, 2,917,384, or 3,111,396. The solutions used for doping contain from 0.05 to 10 weight per cent of a chloride or nitrate of the metal to be deposited. Deposition is conducted using up to seven immersions, each immersion after the first being preceded by a dip in HNO_3, 10 to 50 per cent concentrated. Each immersion is for a period of from 1 to 60 minutes.

Similarly, catalysts are prepared by depositing, as described above, palladium, platinum, iridium, or rhodium by this technique on nickel plated steel wires, and screen where the nickel plate is 1 to 10 mils thick. Similarly, the above deposition techniques are used to prepare noble metal-containing catalysts from Monel, wires, screen saddles, turnings, and foam where the Monel has a composition within the range

Si	0.5–3.5	weight per cent
Mn	0.5–1.5	weight per cent
Fe	3.0	weight per cent maximum
Cu	28–32	weight per cent
Ni	remainder	

For the depositions as described above, the dippings in the noble metal ion containing solutions are conducted with the solution having a temperature of from 20°–100°C.

EXAMPLE VI

To demonstrate emission reduction, an Olds single cylinder engine was used. The engine was run at 1340 RPM and a load was applied by an induction motor to keep the engine speed substantially constant. The fuel employed was clear Indolene; the engine timing was 10° btc.

The engine air flow was about 23.5 lbs per hour. Inlet air temperature to carburetor was 145°C. The A/F ratio was varied from 13.0:1 to 17.0:1 using a knock test engine carburetor. This range of A/F ratios gave fuel times of 85 to 111 seconds per 25 ml of fuel. The catalyst bed was 10 inches from the exhaust port in the head. The exhaust pipe and the catalyst converter were both insulated. The exhaust temperature into the catalyst ranged from 1100°–1200°F. The catalyst converter was filled with the catalyst to be tested and had a capacity of about 22 cubic inches. Another converter which was used had a capacity of 42 cubic inches.

After the engine was warmed up, exhaust gas was sampled before and after the catalyst. The A/F ratio is then varied by adjusting the carburetor and the exhaust sampled again after equilibrium, until the range of A/F ratio is covered by different settings of air fuel ratio. Hydrocarbon concentration is measured by a flame ionization detector. Carbon monoxide and NO_x are measured by non-dispersive infrared. Oxygen is measured polarographically.

Data is given below as per cent reduction for CO, hydrocarbons and NO_x. The value "per cent reduction" is obtained as follows:

$$\text{Percent reduction} = 100 \times \frac{\text{Concentration before catalyst bed} - \text{Concentration after catalyst bed}}{\text{Concentration before catalyst bed.}}$$

In the following table, results for CO, NO_x, and HC (hydrocarbons) are reported for various fuel ratios. Runs 1, 2, and 3 were conducted using a 22 cubic inch capacity catalytic converter. Run 1 was conducted using a foam nickel sample having an average pore size of 30 microns obtained from General Electric. Run 2 was conducted using the palladium containing product of Example I, while Run 3 was conducted using the rhodium containing product of that example. Runs 5, 6, and 7 were conducted using the product of Examples III, IV, and V respectively.

		13.5	14.0	14.5	15.0	15.5	16.0	16.5	Air/Fuel Ratio
1.	Nickel foam	70	73	35	0	0	0	0	NO_x
		0	0	0	7	20	33	42	HC
		0	0	42	40	33	20	14	CO
2.	Nickel foam	29	33	10	12	9	0	0	NO_x
	+ 0.2 per cent	0	3	25	42	29	34	35	HC
	Rh	3	3	25	35	35	50	50	CO
3.	Nickel foam	45	56	28	4	0	0	0	NO_x
	+ 0.3 per	30	54	65	47	40	39	38	HC
	cent Pd	0	0	60	33	20	12	0	CO
4.	*Nickel turn-	60	68	30	0	0	0	0	NO_x
	ings	0	0	0	0	8	16	25	HC
		0	0	0	12	14	30	28	CO
5.	*Nickel turn-	50	61	30	5	0	0	0	NO_x
	ings + 0.1 per	0	5	20	54	45	36	30	HC
	cent Pd	0	2	12	44	34	23	23	CO
6.	*Nickel turn-	55	63	69	2	3	4	0	NO_x
	ings + 0.3	0	14	87	84	83	80	98	HC
	per cent Pd	0	8	60	66	62	58	53	CO
7.	*Nickel turn-	58	67	72	1.7	0	0	0	NO_x
	ings + 0.3	1.2	15	81	85	82	78	76	HC
	per cent Pd	0	9	82	83	90	90	88	CO

*42 cu. in. converter

I claim:

1. A method of depositing a noble metal on a surface of a nickel support, said method comprising contacting said surface of said nickel support with an aqueous solution of a palladium salt having a pH less than 7 until palladium deposition on said surface has substantially ceased;

subsequently contacting the surface thereby produced with nitric acid until said surface is activated, and thereafter

contacting the activated surface thereby produced with an aqueous solution of palladium salt, whereby additional palladium is deposited on said surface.

* * * * *