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FLAME-SPRAYABLE COMPOSITION OF NICKEL COATED MOLYBDENUM

Filed May 27, 1970 3 Sheets-Sheet 1

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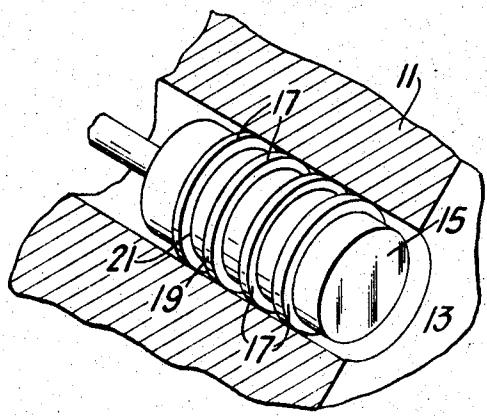

FIG. 1

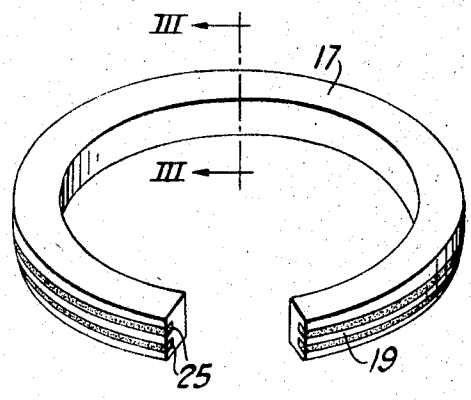

FIG. 2

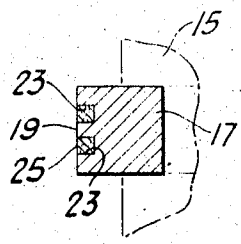

FIG. 3

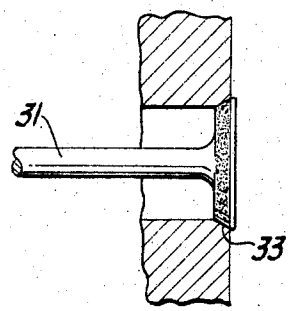

FIG. 5

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FLAME-SPRAYABLE COMPOSITION OF NICKEL COATED MOLYBDENUM

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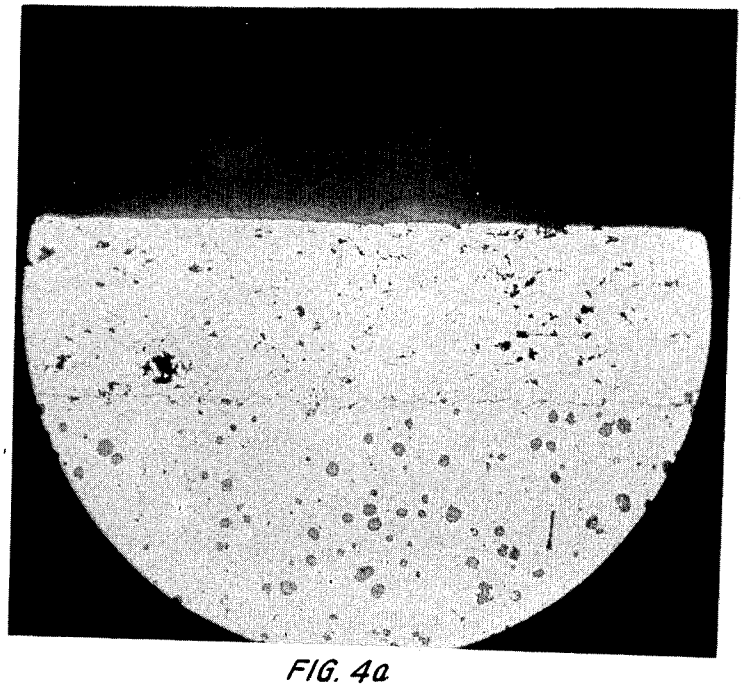

FIG. 4a

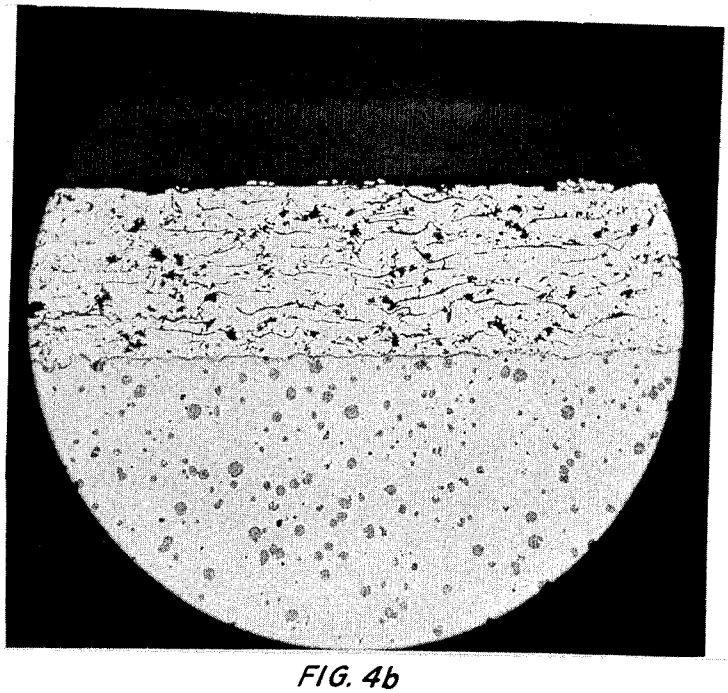

FIG. 4b

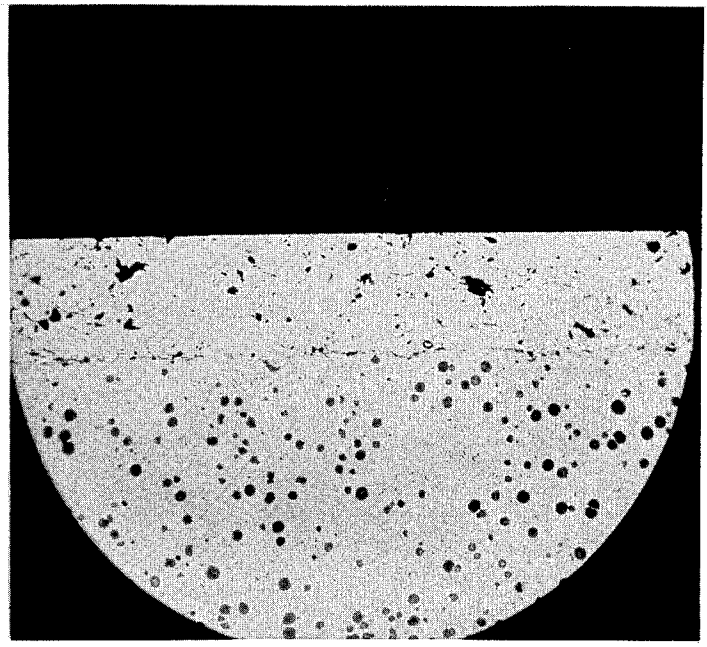

FIG. 4c

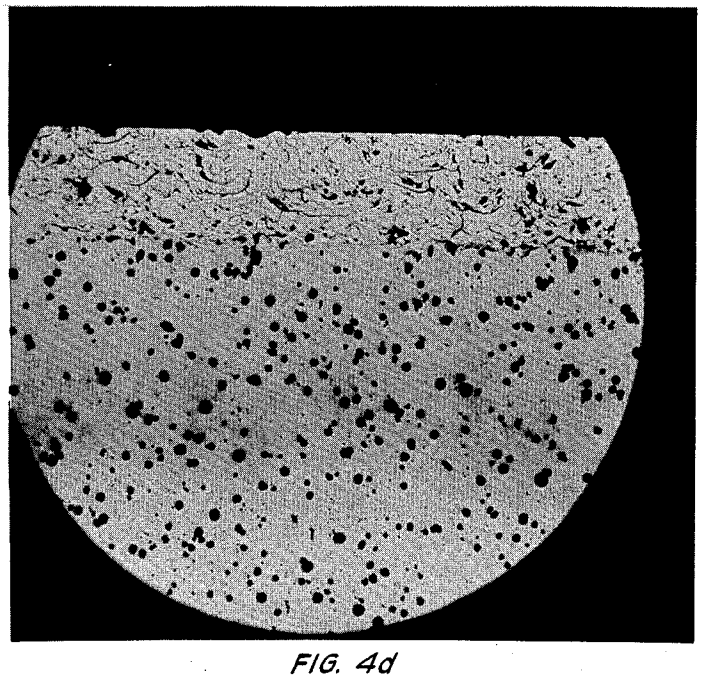

FIG. 4d

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3,843,334

FLAME-SPRAYABLE COMPOSITION OF NICKEL COATED MOLYBDENUM

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U.S. Cl. 29—191.2 17 Claims

ABSTRACT OF THE DISCLOSURE

A flame-sprayable composition comprises a composite of molybdenum particles that are encapsulated with nickel. The composition is applied to a metal substrate with a plasma flame gun to provide a wear-resistant surface on the substrate that maintains its wear-resistance in use at elevated temperatures without a deleterious formation of molybdenum oxides. The composition may be applied to the body of piston rings, exhaust valves and the like that are used in internal combustion engines.

BACKGROUND OF THE INVENTION

This invention relates to a composite of particles that are flame sprayable on a metal substrate to form an adherent, wear-resistant coating, and more particularly to coatings applied to piston rings for use in high-performance internal combustion engines.

Metallurgical wear is the gradual change in the dimensions of a metal part in service under frictional pressure and, thus, it is a primary consideration in high-performance engines.

Wear of metal surfaces may occur from a variety of causes. Because a machined surface almost never has an absolutely true geometric shape and always has a surface roughness resulting from microscopic protrusions extending from the surface, wear will always occur when two metal surfaces engage and slide over each other under a load. At the interface of the two metal surfaces these microscopic protrusions will deform and eventually fracture from the surfaces to become abrasive particles which will further abrade and gouge the engaging surfaces. Similarly, liquids and gas streams flowing over the surface of a metal at high velocities and at high temperatures will deform and remove microscopic protrusions.

Of course, the conditions of wear may be minimized by the use of lubricants. When a lubricant is employed between the wearing surfaces of engaging metal parts, the film thickness of the lubricant if it exceeds the heights of the microscopic protrusions will significantly reduce the conditions of wear so long as the abrasive particles do not bridge the film thickness of the lubricant between the wearing surfaces.

During the reciprocation of a piston in an internal combustion engine, the piston rings carried by the piston engage the cylinder walls of the engine and are slidable thereon whereby wear occurs on both the cylinder walls and the piston rings. Because the purpose of piston rings is to maintain a seal between the piston and cylinder wall during the operation of the engine the conditions accelerating wear must be minimized. Failure of piston rings to properly seal the piston and the cylinder results in gas leakage between the rings and the cylinder wall thereby causing low engine compression, bad ignition, incomplete combustion, and generally accelerated erosion of the piston rings and of the cylinder wall.

DESCRIPTION OF THE PRIOR ART

The wearing surfaces, therefore, of the piston rings are coated with a variety of abrasion-resistant materials to reduce wear; they are generally classed by those skilled

in the art into two major catagories: (1) corrosion-resistant break-in coatings which improve the life and running capabilities of the coated ring itself, and (2) wear-resistant coatings which increase the operating life of the piston ring. This invention relates to the coatings of the latter catagory.

Some wear-resistant coatings include "chromium-plated" surfaces and molybdenum flame-sprayed coatings. Chromium-plated and molybdenum-coated piston rings have not performed well when exposed to elevated temperatures. The molybdenum coating has good anti-scuff wear properties at temperatures less than 450° F.; however, the wear properties of molybdenum coatings deteriorate when the coated surfaces are subjected to high temperatures in excess of 450° F. generated in the engine. Oxidation of the molybdenum coatings occurs at about the threshold temperatures of 450° F. and at temperatures in excess thereof the degree of oxidation increases wherein molybdenum oxides are formed along the grain boundaries of the molybdenum coating. Consequently, the molybdenum coating becomes stratified with the molybdenum oxides precipitated out onto the grain boundaries thereby reducing the over-all strength of the molybdenum coating.

Elemental nickel metal flame-sprayed coatings are unknown in the art because elemental nickel coatings have poor wear-resistant properties. Thus, the combination of molybdenum and nickel would expectedly, when flame-sprayed onto a piston ring, produce a more inferior coating than presently known in the art.

Quite surprisingly, I have discovered a novel composition for a flame-sprayable coating material, which, although using elemental molybdenum, does not form molybdenum oxides in the grain boundaries of the composition and, although using elemental nickel, has excellent wear-resistant properties. The novel composition is a hard and a good wear-resistant material. When my composition is flame-sprayed onto a piston ring made of cast iron, mild steel, or stainless steel, a mechanical and atomic bond is formed between the coating particles and the base of the piston ring.

SUMMARY OF THE INVENTION

In accordance with the invention a flame-sprayable composition or powder comprises discrete particles consisting essentially of a nucleus of molybdenum and of a coating layer of nickel. The composition may be applied to a metal substrate by a plasma flame gun to form a coating that is firmly bonded to the metal substrate to provide a wear-resistant coating at temperatures in excess of 450° F.

DESCRIPTION OF THE DRAWINGS

In the drawings FIG. 1 is a sectional view of a cylinder with a piston carrying piston rings;

FIG. 2 is a perspective view of a piston ring such as the rings in FIG. 1 to which the novel composition of this invention may be applied;

FIG. 3 is a cross sectional view of a typical piston ring taken at lines III—III of FIG. 2;

FIG. 4, generally, is photomicrographs illustrating the composition of this invention flame-sprayed onto the metal substrate in comparison with a conventional molybdenum composition flame-sprayed onto a metal substrate; and

FIG. 5 is a perspective view of an exhaust valve to which the novel flame-sprayable composition of this invention may be applied.

DETAILED DESCRIPTION OF THE DRAWINGS

In FIG. 1 an engine cylinder **11** having a cylinder wall **13** houses a piston **15** that carries a plurality of piston rings **17** spaced apart from one another, surrounding the piston **15**. The piston rings **17** engage the cylinder wall **13** to form

a tight seal between the cylinder wall **13** and the piston **15**.

The piston ring in FIG. 2 is annular having a rectangular cross section where the outer surface of the ring is a wearing surface **19** for engagement with the cylinder wall **13**. As is well known, the piston ring **17** must possess a sufficient tension to provide a spring pressure against the cylinder wall **13** when the piston **15** is disposed within the cylinder **11** for maintaining a seal therebetween. Conventionally, the piston ring **15** is composed of a conventional cast iron or a conventional mild or low carbon steel or stainless steel. The ring illustrated herein has two grooves **23** machined in the wearing surface **19** into which the novel coating compositions **25** of my invention is deposited by conventional flame-spraying techniques and bonded thereto. Piston rings of different designs, however, may be coated with the composition of my invention, such as, for example, flat face rings without grooves; the side faces of the piston rings may also be coated.

The art of flame-spraying is well known. A plasma flame of a plasma arc gun produces tempertures of approximately 32,000° F. This temperature is achieved by applying electrical energy to a gas mixture (such as a 10 to 1 mixture of nitrogen to hydrogen) which dissociates the gas molecules to an atom stage. (An 8 to 1 mixture of argon to hydrogen has also been successfully used.) The gases are then ionized to produce electrons and charged ions. The electrical energy absorbed by ionization is converted to heat energy by the de-ionization of the gas. The particulate composition is then directed into the plasma flame by a carrier gas such as nitrogen. The particles are propelled by the gas escaping through the nozzle of the gun as a stream of molten particles. The nozzle is aimed at the surface to be coated so that the molten particles impinge thereon. Consequently, the molten particles solidify to provide a continuous, adherent coating on the surface resulting from a combination of mechanical and atomic bonding at the interface between the surface and the particles of the coating.

In accordance with the invention, I have found a novel flame-sprayable composition which is a composition of discrete particles of two elemental metal components, namely molybdenum and nickel. The particles are a clad composite powder comprising molybdenum particles that are surrounded by a jacket of nickel.

The composition of my invention ranges from about 38.0% to 62.5% by weight of molybdenum and by difference about 62.0% to 37.5% by weight of nickel. The molybdenum particles should be commercially pure having an analysis of about 99.5% molybdenum and the purity of the nickel should be about 99.9% nickel. I have found it is critical that the oxygen content of the composite powder be less than 0.15% by weight as oxides in the flame-sprayable composition lower the cohesive strength of the flame-sprayed coating. The preferred composition is 55% by weight molybdenum and 45% by weight nickel, which composition has been found to have good wear capability when deposited by the plasma flame-spraying technique.

I have found that a minimum of 37.5% by weight of nickel is essential for the composition of my invention to provide an adequate high temperature, oxidation-resistant, wear-resistant composition when flame sprayed onto the base of a piston ring. When the amount of the nickel is less than 37.5% by weight, the molybdenum in the coating, when exposed to high temperatures, will form deleterious molybdenum oxides at the grain boundaries of the flame-sprayed composition. Consequently, the flame-sprayed coating on the piston ring body will fall apart in use.

On the other hand, when the amount of nickel exceeds 62.0% by weight the flame-sprayed coating will possess poor wear characteristics in that elemental nickel coatings characteristically have poor wear properties. Thus, one skilled in the art would expect the combination of molybdenum and nickel in a flame-sprayed coating to form at high temperatures deleterious molybdenum oxides and to possess poor wear properties. Quite surprisingly, I have discovered that my flame-sprayable composition has excellent wear properties without the formation of deleterious molybdenum oxides.

The particle size of the composite particles of my invention is critical and I have found that the composite particles having a size from about 5 to about 100 microns is the optimum, practical range. If the particle size of the composite particles is less than 5 microns then vaporization of these composite particles occurs readily and consequently results in a poor deposit of the composite particles onto the piston ring body. If the particle size of the composite particles is greater than 100 microns then these particles do not melt readily thereby causing the resultant coating to have unfused particles as well as clogging the flame-spraying gun.

The relative dimensions of the molybdenum nucleus and of the nickel layer are important features of my invention as the composite particles are manufactured by a rather unique process. Preferably the molybdenum nucleus should range from 5–74 microns in diameter with a nickel layer of about 2 microns in thickness.

In the manufacture of the composite particles of my invention, elemental molybdenum particles (having a size of 5–74 microns) are coated with a uniform layer of elemental nickel by chemical precipitation of elemental nickel onto the molybdenum particles. The nickel coating layer thereby has a uniform layer thickness regardless of the diameter of the molybdenum particles.

Molybdenum particles are suspended in a liquid bath of nickel ammonium sulfate whereby nickel in the nickel ammonium sulfate solution is plated onto the molybdenum particles in accordance with the following chemical expression:

$$Ni(NH_3)SO_4+H_2\rightarrow Ni+(NH_4)SO_4$$

This reaction occurs at pressures of 600–650 p.s.i. and at temperatures of 250–450° F. By the above reaction nickel is plated onto the molybdenum particles at a uniform rate regardless of the particle size of the molybdenum. The residence time of molybdenum particles in this solution determines the thickness of the nickel layer.

Consequently, the larger diameter particles (e.g. 74 microns) of molybdenum contain a smaller percentage of nickel than the smaller diameter particles (e.g. 5 microns) of molybdenum. For example, molybdenum particles having a diameter of 74 microns with a 2 micron layer of nickel has a composition of about 87% by weight of molybdenum and 13% by weight of nickel, whereas a molybdenum particle having a diameter of 5 microns with a 2 micron layer of nickel has a composition of about 19.5% by weight of molybdenum and 81.5% by weight of nickel. I have found that by controlling the particle size or nucleus diameter of molybdenum between about 5 to 74 microns in diameter and applying a 2 micron layer of nickel to the molybdenum in accordance with the above described process the total composition of the composite particles of my invention is maintained between 38.0% and 62.5% by weight of molybdenum and by difference 37.5% to 62.0% by weight of nickel.

It should be noted that a nickel layer of 2 microns has been considered as being preferable since a minimum residence time of the molybdenum particles in the bath of nickel ammonium sulfate is needed to achieve the 2 micron layer of nickel; however, a nickel layer of a greater thickness could be used. Of course, the particle size range of the molybdenum nucleus would need be lesser to provide a total composition within the prescribed limits of my invention. Of course, when a smaller particle size range of molybdenum is used the costs of procuring such a powder are increased because of the demand for a more finely comminuted powder.

Consequently, the critical feature is the volume ratio of molybdenum to nickel. I have found that the average vol-

ume ratio of molybdenum to nickel may vary from approximately 1:2 to approximately 1:7 to provide an average composition between 38.0% to 62.5% by weight of molybdenum and by difference 62.0% to 37.5% by weight of nickel.

Before flame-spraying the metallic wear surface of the piston ring with the composition of this invention the surface of the ring is preconditioned by well-known techniques. Typical preconditioning includes degreasing the metal surface, grit blasting the surface to roughen it and the like.

The molybdenum-nickel composite powder of my invention is flame-sprayed with a plasma arc gun to achieve the desired thickness of the coating. Naturally, the coating thickness will depend upon the geometry of the part to be covered and the type of finish required. However, a coating of approximately .012 inches to .020 inches in thickness is applied. Subsequently, the flame-sprayed coating is ground by conventional means to a finish to about .006 to .008 inches in thickness to provide a crown of about .0002 inches to .0006 inches. The resultant coating is hard and tenacious to the wear surface of the piston ring. The interface between the wear surface **19** and the cylinder wall **13** may be subsequently subjected to temperatures in excess of 450° F. without the oxidation of the molybdenum.

To further illustrate the invention the wear surfaces (the outside diameter) of piston rings were degreased in a conventional manner and grit blasted prior to receiving the subsequently applied flame-sprayed composition. The preferred composition of the invention comprising discrete clad particles having an analyses of 55% molybdenum and 45% nickel by weight was flame-sprayed to the wear surface by a plasma flame gun. As a standard, the wear surfaces of piston rings were likewise degreased and subsequently flame-sprayed with a flame-sprayable composition comprised of a standard composition of conventional 100% molybdenum powder. All of the coated piston rings were then subjected to temperatures of 800° F. in a circulating air furnace at 100 hour intervals up to a total of 1,000 hours of exposure. The 800° F. temperature, a temperature much higher than would ordinarily be encountered in normal internal combustion engine operation, was selected to accelerate the metallurgical changes of the coated rings which occur at lower temperatures over a longer period of time. After each 100 hour interval, the piston rings were removed from the furnace, were examined visually, were measured for hardness of the coating, and were sectioned for micro-evaluation. The hardness data of the coatings having the preferred composition of the invention and having the standard composition are tabulated below:

	Hardness Rockwell 15N	
Time at hundred (100) hour intervals	Invention (Ni-clad molyb-denum nucleus)	Standard (pure molyb-denum)
0	80	74
1	84	83
2	84	84
3	85	82
4	86	83
5	81	84
6	84	81
7	85	81
8	84	82
9	85	82
10	86	82

These hardness tests were conducted in accordance with ASTM specifications E 18–67.

These hardness data indicate that the hardness of both types of coatings increased as the time at the temperature to which the coatings were subjected was increased. The hardness of the preferred composition of the invention increased from an average of 80 to 86 Rockwell 15N, whereas the hardness of the standard composition increased from about 74 to 82 Rockwell 15N. Thus, the preferred composition provides a coating having an initial hardness substantially the same as the hardness of the standard composition after the latter has been exposed to 800° F. for 1,000 hours.

The reason for the unexpected hardness of the novel coating of this invention is not entirely known. It is postulated that the increase in hardness of the preferred composition of the invention results from a phenomena known in metallurgy as a precipitation hardening effect. Precipitation hardening is a hardening of an alloy in which a constituent precipitates from a super-saturated solution. It is believed in accordance with this invention that upon flame-spraying the preferred composition of the invention onto a metal substrate, the composition solidifies into the alpha and delta phases of the molybdenum-nickel system, i.e. a nickel phase and a nickel-molybdenum phase (NiMo), respectively. Upon heating of the coated surface, a gamma phase (Ni_3Mo) precipitates out into the matrix of the composition thereby causing an increase in hardness. Because about 15 minutes are required to flame-spray the composition of the invention onto a metal substrate to provide a coating having a thickness of .012–.015 inches, it is believed that an initial, first-stage precipitation hardening effect occurs in the flame-sprayed coating where the temperature at the interface between the metal substrate and the coating is maintained at about 400° F. or less by periodically directing blasts of air onto the coating. A subsequent, second-stage precipitation hardening effect of the flame-sprayed coating occurs when the coating is subjected to actual service conditions causing a hardness increase which further strengthens the coating, especially its resistance to shear forces caused by sliding friction between the piston and cylinder wall.

An increase in hardness also occurs with the standard pure molybdenum composition. However, it is believed that the mechanism is different. The approximately 100% molybdenum composition, when exposed to an oxidizing environment, forms molybdenum oxides which it is believed increases the hardness of the coating. The formation of oxides, however, is metallurgically deleterious in that the oxides precipitate out onto the grain boundaries of the coating, thereby forming stratas which weaken the cohesive strength of the coating. Consequently, stress cracks are formed in the coating over a period of time which may result in the spalling of the coating. In fact, this behavior has been observed in molybdenum coated piston rings that have been used in internal combustion engines.

It is believed that the composition of this invention deters oxide formation by the presence of nickel encapsulating the molybdenum particles whereby the problem of spalling is avoided. The photomicrographs in FIG. 4 illustrate the oxide formation in the standard composition as contrasted to the absence of oxides in the composition of this invention. These photomicrographs were taken from a transverse cross section of the coated surfaces of both the piston rings coated with the preferred composition of the invention and the standard composition. FIG. 4*a*, illustrating the standard composition (pure molybdenum) before exposure to temperature, shows very few oxides in the matrix of the coating. FIG. 4*b*, illustrating the standard composition after 1,000 hours at 800° F., shows a highly stratified coating wherein the oxides of molybdenum have precipitated into layers in the coating. Such a coating as earlier mentioned is subject to spalling, cracking and the like, and is, hence, undesirable for purposes of providing a wear surface on piston rings. FIG. 4*c*, illustrating the preferred composition of the invention before exposure to temperature, shows very few oxides in the coated surface, as would be expected. However, FIG. 4*d*, illustrating the preferred composition of

the invention after exposure to 800° F. for 1,000 hours, unexpectedly shows very little change in the coating; in which few, if any, oxides have formed. Hence, the composition of my invention deters the formation of oxides; the hardness increases due to the precipitation hardening behavior earlier described. Thus, the composition of the invention is better suited for internal combustion engines than the standard 100% molybdenum composition which heretofore has conventionally been used to coat the surfaces of piston rings.

As an example of the invention particles of molybdenum clad with nickel were prepared. The particles were analyzed to be 55.75% by weight of molybdenum and 44.25% by weight of nickel. A screen analysis showed the particles to have the following particle size distribution:

Microns:	Percent by weight
Greater than 105	.24
Greater than 74	20.41
Greater than 53	47.90
Greater than 44	24.09
Greater than 5	7.15
Less than 5	1.21
	100.00

The piston rings which had an inside diameter of 4.9 inches and an outside diameter of 5.4 inches were degreased and grit blasted before receiving this flame-sprayable composition. This composition was flame-sprayed onto the wear surface (outside diameter) of the piston rings. The coating after the flame-spraying had a thickness ranging from .012–.014 inches. This coating was subsequently ground by conventional techniques to .006–.008 inches in order to provide a crown of about .0002 inches on the wearing surface of the piston ring.

The rings were then subjected to the dry brake-shoe test at room temperatures under non-lubricated conditions. This test is used to evaluate the dry wear properties of the coated piston rings which provides an excellent indication of the expected performance of such piston rings when placed into operation in conventional internal combustion engines. The dry brake-shoe test is coducted in a specially designed testing apparatus. The coated piston rings are sectioned into one inch sections. Each section is placed with its coated surface in contact with a rotating drum that is composed of a pearlitic gray cast iron having a hardness ranging from 450 to 500 Bhn. The drum is rotated at about 1600 s.f.m. A load of about 5 pounds is exerted upon the specimen in contact with the rotating drum. Wear tests evaluations are made on the basis of the weight loss of the specimen and the drum and visual observation of the specimen and the drum for such occurrences are scuffing, scoring, and the like.

The average weight loss measured with the specimens of this example, ranged from 3.4 mg. to 1.6 mg. The average weight loss of the drum ranged from 3.8 mg. to 2.7 mg. Visual examination indicated very fine scoring and excellent wear compatability between the specimen and the drum resulting in a good rating. In contrast piston rings that were coated with a pure 100% molybdenum composition having a coating thickness of .006–.008 inches were similarly tested in the dry brake-shoe test and found to have an average specimen weight loss of about 5 mg. and an average drum weight loss of about 10 mg. Visual examination of the pure 100% molybdenum coated piston rings indicated fine scoring and incipient scuffing resulting in a generally fair to poor rating.

Thus, the flame-sprayable composition of my invention may be flame-sprayed onto the body of piston rings, particularly to the wear surface **19** as illustrated in FIGS. 2 and 3, or onto the body of automotive exhaust valves, particularly the seating area **33** of exhaust valves **31** as illustrated in FIG. 5.

In FIG. 5 the seating area **33** of exhaust valve **31** has the novel composition of my invention flame-sprayed thereon to a desired coating thickness. The flame-spraying of my novel composition onto the body of the exhaust valves is especially desirable in that the automobile industry has discovered that the removal of tetraethyl lead from gasoline significantly reduces air pollution caused by the exhaust fumes of an automobile; yet, it has discovered that the removal of tetraethyl lead from gasoline significantly increases the erosion of the seating area of exhaust valves. It has been found that flame-spraying a 100% pure molybdenum powder onto the seating area of exhaust valves is not useful in deterring the erosion of exhaust valves in that, as heretofore explained, deleterious molybdenum oxides form at elevated temperatures above 450° F. By flame-spraying my novel composition onto the body of exhaust valves the erosion of exhaust valves due to the absence of tetraethyl lead from gasoline will be significantly reduced.

While the composition of this invention is preferably in the form of composite particles consisting essentially of a molybdenum nucleus and of a coating layer of nickel, the composition of this invention may also be in the form of a mere mechanical admixture consisting essentially of discrete particles of molybdenum and of discrete particles of nickel having a size range from about 7 to about 100 microns and the composition of such mechanical admixture being about 62.5% to 38.0% by weight of molybdenum and by difference 37.5% to 62.0% by weight of nickel.

What is claimed is:

1. A flame sprayable composition comprising discrete particles consisting essentially of a nucleus of molybdenum and a coating layer of nickel wherein the composition of the particles is from about 62.5% to 38.0% by weight molybdenum and by difference 37.5% to 62.0% by weight nickel.

2. A flame sprayable composition as in Claim **1** wherein the discrete particles have a diameter of from about 7 microns to 100 microns.

3. A flame sprayable composition as in Claim **1** wherein the average volumetric relationship of the molybdenum nucleus to the nickel coating layer is between about 1:2 to 1:7.

4. A flame sprayable composition as in Claim **1** wherein the molybdenum nucleus has a diameter of from about 5 microns to 74 microns and the nickel coating layer has a thickness of about 2 microns.

5. A flame sprayable composition as in Claim **1** wherein the composition of the particles is about 55% by weight molybdenum and 45% by weight nickel.

6. A flame sprayable composition as in Claim **2** wherein the composition of the particles is about 55% by weight molybdenum and 45% by weight nickel.

7. A flame sprayable composition comprising discrete particles consisting essentially of a nucleus of molybdenum and a coating layer of nickel wherein the composition of the particles is from about 62.5% to 38.0% by weight molybdenum and by difference 37.5% to 62.0% by weight nickel and wherein the discrete particles have a diameter of from about 7 microns to 100 microns and wherein the average volumetric relationship of the molybdenum nucleus to the nickel coating layer is between 1:2 to 1:7.

8. A flame sprayable composition as in Claim **7** wherein the composition of the particles is about 55% by weight molybdenum and 45% by weight nickel.

9. A flame sprayable composition comprising an admixture of particles consisting essentially of discrete particles of molybdenum and discrete particles of nickel wherein the discrete particles have a diameter of from about 7 microns to 100 microns and wherein the composition is from about 62.5% to 38.0% by weight molybdenum and by difference 37.5% to 62.0% by weight nickel.

10. A coated metal substrate in which the coating comprises a flame sprayed composition comprising discrete particles consisting essentially of a nucleus of molybdenum and a coating layer of nickel wherein the com-

position of the particles is from about 62.5% to 38.0% by weight molybdenum and by difference 37.5% to 62.0% by weight nickel.

11. A coated metal substrate as in Claim **10** wherein the metal substrate is a piston ring.

12. A coated metal substrate as in Claim **10** wherein the metal substrate is an exhaust valve.

13. A coated metal substrate as in Claim **10** wherein the discrete particles have a diameter of from about 7 microns to 100 microns.

14. A coated metal substrate as in Claim **10** wherein the composition of the particles is about 55% by weight molybdenum and 45% by weight nickel.

15. A coated metal substrate in which the coating comprises a flame sprayed composition comprising discrete particles consisting essentially of a nucleus of molybdenum and a coating layer of nickel wherein the composition of the particles is from about 62.5% to 38.0% by weight molybdenum and by difference 37.5% to 62.0% by weight nickel and wherein the discrete particles have a diameter of from about 7 microns to 100 microns and wherein the average volumetric relationship of the molybdenum nucleus to the nickel coating layer is between 1:2 to 1:7.

16. A coated metal substrate as in Claim **15** wherein the metal substrate is a piston ring.

17. A coated metal substrate as in Claim **16** wherein the metal substrate is an exhaust valve.

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