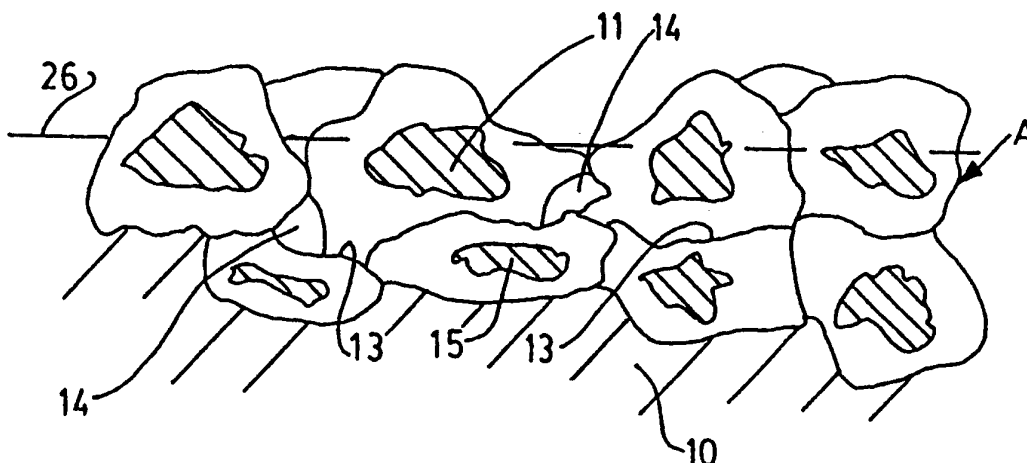




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(54) Title: METAL ENCAPSULATED SOLID LUBRICANT COATING SYSTEM



(57) Abstract

The invention is directed to a thermally sprayable powder having grains comprising: a core of solid lubricant particles comprised of at least graphite and MoS₂ (others may include Bn, NaF, LiF, CaF₂, and WS₂); and a thin, soft metal shell (Ni, Co, Fe, Zn, Sn, Mg, or Cu) encapsulating such core. Some core particles may also be hard, wear-resistant particles from the group consisting of SiC, NiCrAl, FeMn, FeCrAl, FeWNiVCr, NiCrMoVW, FeCrMoVW, CoFeNiCrMoVW, NiCrMoV, and CoMoCrVW. The invention also discloses a solid lubricant coating system for a metal wear interface subject to high temperatures and wet lubrication, comprising: (a) particles of an oil-attracting solid lubricant mixture having at least graphite and MoS₂, (b) soft metal shells encapsulating the particles and being fused together to form a network of grains constituting a coating fusably adhered to the metal interface, the coating having a porosity of about 2-10 % by volume. Further, the invention discloses a method of making an anti-friction coating on metal surfaces such as cylinder bore walls of an engine.

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METAL ENCAPSULATED SOLID LUBRICANT COATING SYSTEM

This invention relates to fluid lubricated metal wear interfaces or contacts, and more particularly to the use of anti-friction solid film lubricants for such interfaces modified to withstand high unit scraping or bearing loads at high temperatures while functioning with either full or partial fluid lubrication.

The utility of certain solid film lubricants for bearings has been known for some time. U.S. patent 1,654,509 (1927) discloses use of powder graphite trapped or covered by a metal binder (i.e., iron, aluminium, bronze, tin, lead, babbitt, or copper) to form a thick coating; all of the metal is heated to at least a thermoplastic condition by melting or arc spraying to bury the graphite. The coating offers limited friction reducing characteristics. Unfortunately (i) the graphite is not exposed except by significant wear of the metal, thus never realising significantly lower friction; (ii) the metal is in a molten condition prior to trapping or burying the graphite causing thermal effects and distortions; and (iii) oxides of the metal serve as the primary lubricant. The prior art has also appreciated the advantage of thermally spraying (by oxy-fuel) aluminium bronze as a solid film lubricant onto cylinder bore surfaces of an engine as demonstrated in U.S. patent 5,080,056. The lubricating quality of such coating at high temperatures is not satisfactory because (i) it lacks compatibility with piston ring materials which usually comprise cast iron, molybdenum coated cast iron, or electroplated hard chromium; and (ii) thermal spraying of the material by oxy-fuel is not desirable because of very high heat input necessitating elaborate tooling to rapidly dissipate heat to avoid distortion of its coated part.

One of the coauthors of this invention has previously disclosed certain solid lubricants operable at high temperatures, but designed for interfacing with

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ceramics, not metals, and generally at low load applications in the absence of any liquids. One solid lubricant disclosed comprised graphite and boron nitride in a highly viscous thermoplastic polymer binder spread in a generous
5 volume onto a seal support comprised of nickel and chromium alloy. The formulation was designed to provide a hard coating which softens at the surface under load while at or above the operating temperature and functioning only under dry operating conditions. Thermoplastic polymer based
10 formulations are unsatisfactory in meeting the needs of a loaded engine component, such as a cylinder bore, because the unit loads are significantly higher (approaching 500 psi), and the surface temperatures are higher, causing scraping. Another solid lubricant disclosed was halide
15 salts or MoS_2 (but not as a combination) in a nickel, copper, or cobalt binder; the coating, without modifications, would not be effective in providing a stable and durable anti-friction coating for the walls of an internal combustion cylinder bore, because the formulations
20 were designed to operate under dry conditions and against ceramics, primarily lithium aluminium silicate and magnesium aluminium silicate, and, thus, the right matrix was not used nor was the right combination of solid lubricants used. Particularly significant is the fact that the formulations
25 were designed to produce a ceramic compatible oxide (e.g., copper oxide or nickel oxide) through partial oxidation of the metal in the formulation. These systems were designed to permit as much as 300-500 microns wear. In the cylinder bore application, only 5-10 micron wear is permitted.

30 It is an object of this invention to provide a plasma sprayable powder for coating a light metal (e.g., alloys of either aluminium, magnesium, or titanium with silicon, zinc, or copper, etc.) cylinder bore surface of an internal combustion engine, the powder having a soft metal
35 encapsulating certain selected solid lubricant particles therein (CaF_2 , MoS_2 , LiF), and, optionally, having soft metal encapsulating hard, wear resistant particles. The

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encapsulation promotes improved fusion to the light metal bore surface and promotes a lace-like network of fusion metal between particles.

The coating composition embodying the invention economically reduces friction for high temperature applications, particularly along a cylinder bore wall at temperatures above 700°F when oil lubrication fails or in the presence of oil flooding (while successfully resisting conventional or improved piston ring applied loads).

10 A method embodying the invention is a low cost method of making coated cylinder walls by rapidly applying a coating by plasma spraying requiring less energy and at reduced or selected areas of the bore wall while achieving excellent adherence and precise deposition with a larger
15 powder grain size, the method demanding less rough and machine finishing of the bore surface.

An aluminium alloy cylinder wall of an engine which is coated with a coating of the present invention has the advantages that it (i) assists in achieving reduced piston
20 system friction and reduced piston blow-by, all resulting in improved vehicle fuel economy of 2-4% for a gasoline powered vehicle; (ii) reduces hydrocarbon emissions; and (iii) reduces engine vibration by at least 20% at wide-open throttle conditions at moderate speeds (i.e., 1000-3000
25 rpm).

The invention, in a first aspect, is a thermally sprayable powder, having powder grains comprising: (a) a core of solid lubricant particles comprising at least graphite and MoS_2 ; and (b) a thin, soft metal shell
30 encapsulating such core. Additional powder grains can comprise other solid lubricants of the group consisting of hexagonal BN, LiF, CaF_2 , WS_2 , and eutectic mixtures of LiF/ CaF_2 or LiF/ NaF_2 ; additional powder grains can comprise hard, wear-resistant particles selected from the group
35 consisting of SiC, NiCrAl, and intermetallic compounds such as FeWNiVCr, NiCrMoVW, DeCrMoVW, CoFeNiCrMoVW, NiCrMoV, and CoMoCrVW (known as laves phase). The soft metal for the shell

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is selected from the group consisting of Ni, Co, Cu, Zn, Sn, Mg, and Fe.

The invention in another aspect is a solid lubricant coating system for a metal wear interface subject to high temperatures and wet lubrication, comprising: (a) particles of oil-attracting solid lubricants comprised of at least graphite and MoS_2 , (b) soft metal shells encapsulating the particles and being fused together to form a network of grains constituting a coating fusably adhered to the metal interface, the coating having a porosity of 2-10% by volume. The coating has a deposited thickness in the range of 40-250 microns, and is desirably honed to a thickness of about 25-175 microns.

The invention in still another aspect is a method of making an anti-friction coating on a metal surface subject to sliding wear, comprising: (a) forming an encapsulated powder having grains comprising essentially a core of solid lubricants of graphite and MoS_2 , and a thin shell of fusable soft metal; (b) plasma spraying the powder onto a light metal surface to form a coating; and (c) finish-smoothing of the coating to a uniform thickness of about 25-175 microns. The light metal surface is constituted of a metal or alloyed metal selected from the group consisting of aluminium, magnesium, and titanium, the light metal surface being cleansed to freshly expose the light metal or metal alloy just prior to plasma spraying.

Yet another aspect of this invention is an engine block having one or more anti-friction coated cylinder bore walls, comprising: (a) a metal engine block having at least one metal cylinder wall; (b) a coating of grains fused to the cylinder bore wall, the grains each being comprised of solid lubricant particles encapsulated within a soft metal shell, the shells being fused together to form a network with limited porosity, the solid lubricant comprising graphite and MoS_2 ; and (c) wet oil lubrication retained within the porosity of the coating. The soft metal of the coating will have a hardness no greater than 50 Rc

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(preferably Rc 20-30); the soft metal may additionally comprise a small amount of alloy metal adherently compatible with the cylinder bore wall metal.

5 The invention will now be described further, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a highly enlarged view of one type of powder grain embodying this invention;

10 Figure 2 is a view like Figure 1, depicting another powder grain useful with this invention;

Figure 3 is a schematic microscopic view of a segment of the as-deposited coating system of this invention;

15 Figure 4 is a view like that of Figure 3, the coating having been honed and used in a sliding friction application;

Figure 5 is a schematic representation of the forces that influence coulomb friction;

20 Figure 6 is a highly enlarged microscopic view in cross-section of interfacing surfaces showing the irregularities of normal surfaces that affect coulomb friction;

25 Figure 7 is a view similar to Figure 6 showing the incorporation of solid films on the interfacing surfaces that affect coulomb friction;

Figure 8 is a graphical illustration of the onset of plastic flow of surface films as a function of stress and temperature;

30 Figure 9 is a graphical illustration of surface energy (hardness) as a function of temperature for surface films;

35 Figure 10 is a graphical illustration of the coefficient of friction for block graphite as a function of time;

Figure 11 is a graphical illustration of the coefficient of friction and also of wear as a function

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of time for the coating system of this invention tested at the temperature of 500°F;

Figure 12 is a block diagram showing schematically the steps involved in a method aspect of this invention;

5 Figure 13 is an enlarged sectional view of a portion of the liner in position for being installed in a cylinder block bore;

10 Figure 14 is a schematic illustration of the mechanics involved in reciprocating a piston within a cylinder bore showing the travel of the piston rings which promote a loading on the cylinder bore coating system;

15 Figure 15 is a view of the coating apparatus for depositing at high temperatures a plasma coating on a cylinder bore shown in cross-section; and

20 Figure 16 is a cross-sectional illustration of an internal combustion engine containing the product of this invention showing one coated cylinder bore in its environment for reducing the total engine friction, vibration, and fuel consumption for the operation of such engine.

To achieve a significant reduction in the coefficient of friction at high temperatures between normally oil-bathed metal contact surfaces, loaded to at least 10 psi, the coating system cannot rely on graphite or any one lubricant by itself, but rather upon a specific combination of solid lubricant particles encapsulated in soft metal shells that are easily fusable to each other and to the metal of the sliding interface, while retaining a desired porosity.

As shown in Figure 3, the inventive system comprises a layer A of powder grains adhered to a metal substrate or wall 10, each grain possessing a core 11 of solid lubricant particles and a soft metal shell 12 fused to adjacent shells at contact areas 13 resulting in a fused network that possess pores 14. The solid lubricant particles must comprise at least graphite and MoS₂,

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respectively present in the coating A, in amounts of, by weight, 30-70% and 30-90% of the lubricant core. It is desirable to additionally include certain other solid lubricant particles selected from the group consisting of boron nitride, calcium difluoride, lithium fluoride, sodium fluoride, eutectic mixtures of LiF/CaF_2 or LiF/NaF_2 , and tungsten disulfide. When these other solid lubricant particles are present in the coating they should be present in the amount of about 5-20% by weight of the lubricant cores. The cores of certain particles may also be constituted of hard, wear-resistant particles 15, such as selected from the group consisting of silicon carbide, FeCrAl, NiCrAl, or FeCrMn steel and laves phases such as intermetallic compounds of FeWNiVCr, NiCrMoVW, DeCrMoWV, CoFeNiCrMoWV, NiCrMoV, and CoMoCrVW. The wear-resistant particles should be present in a minor amount controlled to be in the range of 5-25% by weight of the total cores. Such wear-resistant particles 15, in such controlled amount, facilitate the following function: when uniformly distributed in submicron size particulates in the grain matrix, they act as load carriers and, with proper honing, produce adjacent relieved areas that retain oil and solid lubricant reservoirs.

The powder, useful as a raw material in creating the coating system, is comprised of powder grains 16 containing a core of solid lubricant (see Figure 1). The grains 16 have a core 17 of solid lubricant surrounded by an encapsulating soft metal shell 18 having a thickness 19 of about 5-40 microns, a volume ratio of the shell to the core in the range of 50:50 to 90:10, and a weight ratio of the shell to the lubricant core in the range of 70:30 to 95:5. The average grain size of the solid lubricant core grains is in the range of about 2-10 microns, and the hardness of the soft metal shell is no greater than Rc 40, preferably Rc 20. The soft metal shells are stable up to a temperature of at least 1200°F when the soft metal shell is selected from the group described above.

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Powder grains 20 have hard, wear-resistant core particles 21 (see Figure 2). Such grains have the wear-resistant core 21 comprised of the materials described above, encapsulated by a soft metal shell 22 (selected as a metal or metal alloy from Ni, Co, Cu, Zn, Sn, Mg, and Fe). Such grains also contribute to the reduction of friction since such metals oxidize on exposure to high temperature; the oxides, such as NiO, CoO, or Cu₂O, have an inherent low coefficient of friction. The thickness 23 of the soft metal shell is in the range of about 5-40 microns or 70-80% of the radial cross-section. The average grain size of the wear-resistant grains 20 is in the range of .2-5.0 microns, the volume ratio of the shell to the core is about 95:5 to 80:20, and the weight ratio is about 95:5 to 70:30.

The encapsulated solid lubricant particles may be created by a treatment wherein the solid lubricants are placed in a molten bath of the soft metal and stirred, and the slurry is then comminuted to form the encapsulated lubricant particles 16. The powder may also be made alternatively by spray drying; to this end, a water-based slurry of very fine particles of soft metal and of the solid lubricants is prepared. The slurry is blended with .5-1.5% by weight water soluble organic binder such as gum arabic and/or polyvinyl alcohol or carbowax. The blended slurry is then atomized by hot spraying into a hot circulating air chamber at or about 300°F. A well-known method of the latter is hydrometallurgical deposition developed and commercially practised by Skeritt-Gordon of Canada.

As shown in Figure 4, the preferred coating, when operatively used, will have a glazed or polished outer surface 24 as a result of engine start-up use or as a result of honing of the deposited particles along a honing line 26 (see Figure 3). The coating will have a predetermined desirable amount of pores 14 which retain fluid oil for additional lubrication. The solid lubricants will be smeared or spread across the honed or polished surface 24 as a result of operative use at the sliding interfaces.

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Friction in an oil-bathed environment will be dependent partly upon fluid friction and the oil film (layers in the fluid sheared at different velocities, commonly referred to as hydrodynamic friction), and, more importantly, dependent on dry or coulomb friction between contacting solid, rigid bodies (also referred to as boundary friction). Dry friction is tangential and opposed to the direction of sliding interengagement. As shown in Figure 5, there is a visualisation of the mechanical action of friction. The weight of a block imposes a normal force N on table C that is spread across several load forces $N-1$ at each interengaging hump 27 (see Figure 6) (attributable to the interatomic bonds of the metal at the surface). The composite of all the tangential components of the small reaction forces $F-1$ at each of the interengaged humps 27 is the total friction force F . The humps are the inherent irregularities or asperities in any surface on a microscopic scale. When the interengaging surfaces are in relative motion, the contacts are more nearly along the tops of the humps and therefore the tangential reaction forces will be smaller. When the bodies are at rest, the coefficient of friction will be greater. Friction is influenced by the deformation and tearing of dry surface irregularities, hardness of the interengaged surfaces, and the presence of surface film such as oxides or oils. As a result, actual friction will be different from idealised perfect contact friction and will depend upon the ratio between shear and yield stresses of the interengaged surfaces. Thus, the presence of a film on each of the interengaging surfaces (see Figure 7) will serve to change the coefficient of friction depending upon the shear and yield stress capacities of the films and their relative hardness. Such films provide for shearing or sliding of boundary layers within the film to reduce friction. Such shearing is localised to essentially the areas where the humps provide hard support for the films. This localisation reduces friction further.

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Friction is also influenced significantly by temperature because high local temperatures can influence adhesion at the contact points. As shown in Figure 8, as temperature goes up, the critical stress for slip goes down, which increases the actual area of contact surface for the same applied load, thereby increasing friction. As shown in Figure 9, as the temperature approaches melting, the hardness (E) goes down.

The influence of temperature is particularly evident on graphite, as shown in Figure 10. The coefficient of friction for block graphite rapidly increases to above .4 at 500°F and above .5 at 800°F, and even higher at 1000°F. The coefficient of friction for graphite at 400°F or lower becomes generally uniform at below .05. Contrast this with the coefficient of friction performance and wear performance of the coating system of this invention represented in Figure 11. It should be noted that the coefficient of friction generally uniformly stays below .1, and wear is generally uniform at about 0.001"/100 hours at 500°F (see Figure 11). The coating for Figure 11 comprises only particles of graphite and boron nitride in a temperature stable polymer.

At least graphite and molybdenum disulfide must be present in the solid lubricant particles in amount of 5-30% by weight of the coating. Graphite, as earlier indicated, is effective as a solid lubricant only up to temperatures around 400°F, and possesses very poor load bearing capability such as that experienced by a piston ring scraping against the graphite itself. Molybdenum disulfide should be present in an amount of 30-100% by weight of the solid lubricants, and, most importantly, is effective in increasing the load bearing capability as well as the temperature stability of the mixture up to a temperature of at least 580°F, but will break down into molybdenum and sulfur at temperatures in excess of 580°F in air or nonreducing atmospheres. Molybdenum disulfide reduces friction in the absence of oil or in the presence of oil,

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and, most importantly, supports loads of at least 10 psi at such high temperatures. Molybdenum disulfide is also an oil attractor and is very useful in this invention, which must deal with wet lubrication.

5 Boron nitride, when selected, should be present in an amount of 5-50% by weight of the solid lubricants, and increases the stability of the mixture up to temperatures as high as 700°F and concurrently stabilises the temperature for the ingredients of molybdenum disulfide and graphite.

10 Boron nitride is an effective oil attractor.

 Calcium difluoride and lithium fluoride are oil attractors, and are stable up to the respective temperatures of 1500°F and 1200°F and resist loads of up to 50 psi or higher. These solid lubricants yield a dry coefficient of
15 friction of 0.1-0.2.

 Porosity allows wet oil to be retained in the pores of the coating as an impregnant during operation of the sliding contacts, particularly when the contacts are between a piston and a cylinder bore wall of an engine. The
20 temperature stability of the coating is important because typical engine cylinder bore walls will experience, at certain zones thereof and under certain engine operating conditions such as failure of coolant or oil pump, temperatures as high as 700°F even though the hottest zone
25 of the cylinder bore surface in the combustion chamber under normal operating conditions is only about 540°F. The optimum solid lubricant mixture will contain lubricants beyond the graphite and molybdenum disulfide. The coefficient of friction for the coating grains in the
30 as-deposited condition will be in the range of .07-.08 at room temperature and a coefficient of friction as low as .03 at 700°F.

 To further enhance the solid lubricant mass beyond the exposed cores and smear film of Figure 4, the coating
35 system may further include an over-layer of a thermoset polymer emulsion containing more solid lubricants. The solid lubricant should comprise particles of at least two of

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graphite, MoS_2 , and BN. The thermoset polymer may be comprised of a thermoset epoxy, such as bisphenol A present in an amount of 25-70% of the polymer, such epoxy being of the type that cross-links and provides hydrocarbon and water vapour transfer to graphite while attracting oil. The polymer also should contain a curing agent present in an amount of about 2-5% of the polymer such as dicyandiamide; the polymer may also contain a dispersing agent present in an amount of .3-1.5% such as 2, 4, 6 tri dimethylamino ethyl phenol.

The emulsion may comprise mineral spirits or butyl acetate that suspend the particles of solid lubricant and polymer. The emulsion may be applied to the substrate or engine bore wall by any variety of techniques, at room temperature, such as emulsion spraying, painting such as by roller, or a tape which carries the emulsion.

The soft metal of the powder shells may incorporate other metal alloying ingredients that are particularly compatible and adherent to the substrate or interface metal material. For example, it would be difficult to fusably adhere pure copper shells to an aluminium substrate; an alloy addition of 4-5% by weight aluminium to the shell metal promotes the needed fusion. It may be desirable to add 3-7% by weight of such alloying metal to the shell metal to promote fusion adhesion.

Method of Making Coated Surfaces

As shown in Figure 12, the comprehensive method of making coated surfaces, such as cylinder bore walls, according to this invention, comprises the steps: (a) forming an encapsulated powder having grains comprising a solid lubricant core of graphite and MoS_2 , and a thin shell of fusable soft metal; (b) plasma spraying the powder onto a cleansed or freshly exposed light metal surface to form a coating; and (c) finish-smoothing of the coating to a thickness of about 25-60 microns.

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Such method provides several new features that should be mentioned here. Plasma sprayed powder (i) will form a controlled porosity that allows for impregnation of wet oil; (ii) the encapsulated powder grains create
5 asperities in the surface such that, when honed, the edges of the shell metal provide a smaller localised area of hard supporting asperities where boundary layer shear will take place in the smeared solid lubricant thereover to further reduce friction (similar to microgrooving), and (ii) the
10 adherent metal network created as a result of melting only the outer skin of the soft metal shells during plasma spraying.

As shown in Figure 13, if a liner is used as the surface to be coated, the liner 30 would be preferably
15 constituted of the same material as that of the parent bore surface 31. However, the liner can be any metal that has a higher strength as the metal of the parent bore wall; this is often achieved by making an alloy of the metal used for the parent bore wall. For example, C-355 or C-356 aluminium
20 alloys for the liner are stronger than the 319 aluminium alloy commonly used for aluminium engine blocks. The liner must have generally thermal conductivity and thermal expansion characteristics essentially the same as the block. Preferably, only the liner 30 is coated interiorly at least
25 at the upper region 32, as will be described subsequently, and the liner then assembled to the parent bore by either being frozen to about a temperature of -40°F while maintaining the parent bore at room temperature, or the parent bore may be heated to 270°F while the liner is
30 retained at room temperature, or possibly a combination of the two procedures. In either case, a shrink-fit is obtained by placing the liner in such differential temperature condition within the parent bore. Preferably, the liner is coated at 33 (at room temperature) on its
35 exterior surface with a copper flake epoxy mixture, the epoxy being of the type described for use in coating. The copper flake within such epoxy coating assures not only an

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extremely solid bond between the liner and the light metal parent bore, but also increases the thermal transfer therebetween on a microscopic scale.

Plasma spraying of the flowable powder is carried
5 out to form an adherent porous layer of powder grains, the powder consisting of particles of solid lubricant encapsulated in a soft metal shell. The flowable powder can be and often is a composite of the solid film lubricant and the soft metal powder produced by spray drying in which a
10 combustible, ash-free, organic binder (such as 1% carbowax) and/or 0.5% gum arabic are used to produce the slurry from which the spray-dried powder is produced. Secondly, the coating is honed to a thin thickness 34 of about 25-60 microns to expose the core solid lubricants at 35 as well as
15 present shell edges 36 which additionally provide lubricating qualities (see Figure 4).

It is desirable to not only have powder grains of solid lubricant encased in a soft metal shell, such as nickel, but also powder grains of a solid hard metal such as
20 FeCrMn or FeMn. The outer shells of these two different grains will melt and alloy fuse during plasma spraying to create an even harder alloyed metal network such as FeCrNiMn and FeNiMn.

The coating is plasma sprayed onto the substrate in
25 a deposited thickness range of about 40-140 microns. The substrate surface is preferably cleansed to provide fresh metal prior to plasma spraying, or is given a phosphate pretreatment. The surface is prepared by degreasing with OSHA approved solvent, such as ethylene dichloride, followed
30 by rinsing with isopropyl alcohol. The surface is grit blasted with clean grit. Alternately, the surface can be cleaned by etching with dilute HF and followed by dilute HNO_3 and then washed and rinsed. Wire brushing also helps to move the metal around without burnishing. The flowable
35 powder useful for such plasma spraying preferably has an average particle size in the range of 20-75 microns, but for practical high volume production, such range should be

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restricted to 30-55 microns. Grains of 30-55 microns are freely flowable, which is necessary for feeding a plasma gun. If less than 30 microns, the powder will not flow freely. If greater than 55 microns, stratification will
5 occur in the coating lacking uniform comingling of the particles. This does not mean that particle sizes outside such range must be scraped for an economic loss; rather, the finer particles can be agglomerated with wax to the desired size and oversized particles can be ball-mixed to the
10 desired size. Thus, all powder grains can be used.

The solid lubricants, which form the core of such encapsulated grains, are of the previously described class of graphite, molybdenum disulfide, and additionally may contain calcium fluoride, sodium fluoride, lithium fluoride,
15 boron nitride, and tungsten disulfide. The soft metal shell is selected from the class of nickel, boron, cobalt, and iron, or alloys of such selected metal.

It is, in most cases, necessary to coat only a segment of the entire cylinder bore surface. As shown in
20 Figure 14, the location of conventional sliding piston rings 37 moves linearly along the bore wall 31 a distance 38. The locus of the piston ring contact with the coating is moved by the crank arm 39 during an angle representing about 60° of crank movement. This distance is about one-third of the
25 full linear movement 40 of the piston rings (between top dead centre--TDC, and bottom dead centre--BDC). The distance 38 represents the hot zone of the bore wall where lubrication can vary and the bore wall is most susceptible to drag and piston slap, and which is the source of a
30 significant amount of engine friction losses while causing scuffing of the bore wall in case of wet lubricant failure. When the coating is limited to a segment of the bore wall depth, it is desirable to use an overlayer of an organic polymer with solid lubricant over the shortened coating as
35 well as the rest of the bore. A discontinuity or step may be created between the shortened coating and the parent bore wall; such a step can cause piston ring instability. Honing

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of the step reduces its severity, but the overlayer will eliminate or reduce any step.

Plasma spraying may be carried out by equipment, as illustrated in Figure 15, using a spray gun 41 having a pair of interior electrodes 42, 43 that create an arc through which powdered metal and inert gas are introduced to form a plasma. The powder metal may be introduced through a supply line 44 connected to a slip ring 45 that in turn connects to a powder channel 46 that delivers to the nozzle 47. The plasma heats the powder, being carried therewith, along the shells of the powder only. The gun is carried on an articulating arm 48 which is moved in a combined circular linear movement by a journal 49 carried on an eccentric positioner 51 which in turn is carried on a rotating disc 50 driven by a motor 52. The nozzle 47 of the gun is entrained in a fixed swivel journal 53 so that the spray pattern 54 is moved both annularly as well as linearly up and down the bore surface 55 as a result of the articulating motion of the gun.

Yet another aspect of this invention is the completed product resulting from the practice of the method and use of the chemistry described herein. As shown in Figure 16, the product is an engine block 60 having one or more anti-friction coated cylinder bore walls 61, comprising a coating 62 of powder grains fused to the cylinder bore wall 61, the grains being comprised of at least solid lubricant particles encapsulated within a soft metal shell, said shells being fused together to form a network with limited porosity, the solid lubricant comprising graphite and MoS_2 ; and wet oil lubrication retained within the porosity of the coating. The soft metal of the coating should have a hardness no greater than 60 Rc. The metal of the cylinder wall is preferably selected from the group of aluminium, titanium, magnesium, and alloys of such metals with copper, zinc, or silicon. The soft metal again may additionally comprise a small amount of alloy metal adherently compatible with the cylinder bore wall metal.

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Such product is characterised by a reduction in engine friction resulting from reduction of piston system friction of at least 25% because of the reduction in boundary layer friction as well as the ability to operate
5 the engine with a near zero piston/cylinder bore clearance. Furthermore, such product provides for a reduction in engine hydrocarbon emissions by at least 25% because of the adaptation of the piston ring designs, disclosed in concurrently filed patent applications, and thereby reduce
10 the top land crevice volume. The blow-by of the engine (combustion gases blowing past the piston rings) is reduced also by about 25% because of the near zero clearance combined with the piston ring design just cited. The temperature of the coolant used to maintain proper
15 temperature of the engine can be reduced by 20°F because a significantly lower viscosity oil can be used with such change. The oil temperature can be reduced by at least 50°F when coupled with the avoidance of tar deposit formation on the combustion chamber surfaces, and an increase in the
20 compression ratio of the engine by at least one with attendant improvement in fuel economy and power.

Another significant aspect of the coated block, in accordance with this invention, is the ability for resisting formic acid, formed when using flex fuels containing
25 methanol. Typically, an engine would have its surfaces degrade at 20,000 miles or greater as a result of the formation of formic acid under a peculiar set of engine conditions with such flex fuels. With the use of the coated bore walls as herein, such resistance to formic acid
30 corrosion is eliminated. Moreover, the coated product obtains greater accuracy of roundness within the cylinder bore as the conventional rings ride thereagainst, contributing to the reduction in blow-by and friction as mentioned earlier. Friction reduction is obtained due to a
35 reduction in the boundary friction component as well as the reduction in the boundary/dry friction coefficient itself.

- 18 -

The coated block plays an important role in the overall operation of engine efficiency. As shown in Figure 16, the block has an interior cooling jacket 63 along its sides and cooperates to receive a head 64 containing intake and exhaust passages 65, 66 opened and closed by intake and exhaust valves 67, 68 operated by a valve train 69 actuated by camshafts 70. The combustible gases are ignited by spark ignition 71 located centrally of the combustion chamber 72 to move the piston 73, which in turn actuates a connecting rod 74 to turn a crankshaft 75 rotating within a crank case 76. Oil is drawn from the crank case 76 and splashed within the interior of the block to lubricate and bathe the piston 73 during its reciprocal movement therein. The cooling fluid circulates about the cylinder bore wall to extract heat therefrom, which influences the efficiency of the engine by reducing the heat input into the air/fuel charge during the intake stroke, and thus increases volumetric efficiency as well as power and fuel economy.

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- 19 -

CLAIMS

1. A thermally sprayable powder, having grains of
5 the powder comprising essentially:
 (i) a core (11,17,21) of solid lubricant particles
 comprising graphite and MoS_2 ;
 (ii) a soft metal shell (12,18,22) encapsulating said
 core.
10
2. A powder as claimed in claim 1, in which other
grains of the powder comprise cores of at least one solid
lubricant of the group consisting of hexagonal BN, LiF,
 CaF_2 , WS_2 , and eutectic mixtures of LiF/ CaF_2 or LiF/NaFe.
15
3. A powder as claimed in claim 1, in which other
grains of said powder comprise particles of wear-resistant
material as at least one of the core or the entire grain.
- 20 4. A powder as claimed in claim 3, in which said
wear-resistant material is selected from the group
consisting of SiC, FeMn, FeCrAl, NiCrAl, FeWNiVCr, NiCrMoVW,
FeCrMoWV, CoFeNiCrMoWV, NiCrMoV, and CoMoCrVW.
- 25 5. A powder as claimed in claim 1, in which said
soft metal is a metal or an alloy of at least one selected
from the group consisting of Ni, Co, Cu, Zn, Sn, Mg, and Fe.
6. A powder as claimed in claim 5, in which said
30 shell has a hardness no greater than about Rc 50.
7. A powder as claimed in claim 5, in which said
soft metal is designed to be fusably adhered to a metal
substrate, said soft metal containing a small amount of
35 bonding metal that alloys with said substrate metal.

- 20 -

8. A powder as claimed in claim 7, in which said soft metal is present in an amount of 30-90% by weight of the powder.

5 9. A powder as claimed in claim 1, in which said shell has a thickness of about 5-40 microns.

10 10. A solid lubricant coating system for a metal wear interface subject to high temperatures and wet lubrication, comprising:

(a) particles of an oil-attracting solid lubricant comprised of at least graphite and MoS_2 ; and

(b) soft metal shells encapsulating said particles and being fused together to form a network of grains
15 constituting a coating fusably adhered to said metal interface, said coating having a porosity of at least 2-10% by volume.

11. A system as claimed in claim 10, in which said
20 coating system additionally includes hard wear-resistant material encapsulated by soft metal shells or fusably alloyed to the shells of the solid lubricant particles.

12. A system as claimed in claim 11, in which said
25 wear-resistant particles are selected from the group consisting of SiC, FeMn, FeCrAl, NiCrAl, FeWNiVCr, NiCrMoVW, FeCrMoWV, CoFeNiCrMoWV, NiCrMoV, and CoMoCrVW.

13. A system as claimed in claim 10, in which said
30 solid lubricant comprises additionally at least one of hexagonal BN, CaF_2 , LiF, WS_2 , and eutectic mixtures of LiF/ CaF_2 or LiF/ NaF_2 .

14. A system as claimed in claim 10, in which said
35 soft metal has a hardness not exceeding Rc 50, and is selected from the group consisting of Ni, Co, Cu, Zn, Sn, Mg, and Si.

- 21 -

15. A system as claimed in claim 10, in which said coating has an as-deposited thickness in the range of 40-250 microns.

5 16. A system as claimed in claim 11, in which said coating is honed to a thickness of about 25-175 microns.

17. A system as claimed in claim 10, in which said metal interface is a light metal or its alloy selected from
10 the group consisting of Al, Mg, and Ti.

18. A system as claimed in claim 10, in which said solid lubricants are present in said coating in an amount of 5-60% by weight.

15

19. A system as claimed in claim 17, in which said shells comprise an alloy of said soft metal and the interface metal, said interface metal being present in said shells in an amount no greater than 7% by weight.

20

20. A system as claimed in claim 10, in which said graphite constitutes 5-70% by volume of said solid lubricants and said MoS₂ constitutes 5-90% by volume of said solid lubricants.

25

21. A method of making an anti-friction coating on a metal surface subject to sliding wear, comprising:

(a) forming a powder having grains comprising a core of solid lubricant of graphite and MoS₂ and a thin
30 shell of fusible soft metal;

(b) plasma spraying said powder onto a light metal surface to form a coating; and

(c) finish-smoothing said coating to a uniform thickness of about 25-175 microns.

35

22. A method as claimed in claim 21, in which said coating is deposited in a thickness range of 40-250 microns.

- 22 -

23. A method as claimed in claim 21, in which said metal surface is a light metal cleansed to freshly expose the light metal just prior to plasma spraying.

5 24. A method as claimed in claim 23, in which said cleansed light metal surface is given a phosphate pretreatment.

25. A method as claimed in claim 21, in which said
10 light metal surface is a cylinder bore wall of an internal combustion engine.

26. A method as claimed in claim 25, in which said bore wall is a liner inserted into the block of said engine
15 or cast-in-place.

27. A method as claimed in claim 21, in which said powder grains have an average size in the range of 25-55 microns.
20

28. A method as claimed in claim 21, in which said solid lubricants additionally comprise at least one of hexagonal BN, CaF_2 , LiF, WS_2 , and eutectic mixtures of LiF/ NaF_2 or LiF/ CaF_2 .
25

29. A method as claimed in claim 21, in which said light metal is selected from the group consisting of Al, Ti, Mg, or an alloy of such metal with Sn, Zn, Cu, and Si.

30 30. A method as claimed in claim 21, in which said plasma has a temperature of at least 1200°C.

31. A method as claimed in claim 21, in which said powder further comprises grains of wear-resistant material
35 residing either as cores of material in a soft metal shell or as the entire grain, and said smoothing is carried out by honing.

- 23 -

32. A method as claimed in claim 21, in which a thin emulsion layer of solid lubricant particles and a thermoset polymer is deposited over said smoothed coating.

5 33. A method as claimed in claim 32, in which said solid lubricant particles of said layer comprise at least two selected from the group of graphite, BN, and MoS₂.

34. An engine block having one or more
10 anti-friction coated cylinder bore walls, comprising:

(a) a metal engine block having at least one metal cylinder wall;

(b) a coating of grains fused to said cylinder bore wall, said grains having solid lubricant particles
15 encapsulated within a soft metal shell, said shells being fused together to form a network with limited porosity, said solid lubricant comprising graphite and MoS₂; and

(c) wet oil lubrication retained within the porosity of said coating.

20

35. An engine block as claimed in claim 34, in which said network also includes wear-resistant material fused and alloyed to the shells of said solid lubricant particles.

25

36. An engine block as claimed in claim 34, in which said soft metal has a hardness no greater than 50 Rc.

37. An engine block as claimed in claim 34, in
30 which said soft metal is selected from the group of Ni, Co, Cu, Zn, Sn, Mg, and Fe.

38. An engine block as claimed in claim 34, in which the metal for said cylinder wall is a metal or alloyed
35 metal selected from the group of Al, Mg, Ti, and said soft metal additionally comprises a small amount of alloyed metal adherently compatible with said cylinder bore wall metal.

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39. An engine block as claimed in claim 34, in which said solid lubricant smears and spreads across said cylinder wall during engine use.

5 40. An engine block as claimed in claim 34, in which a thin layer of solid lubricant encased in a thermoset polymer resides on said coating.

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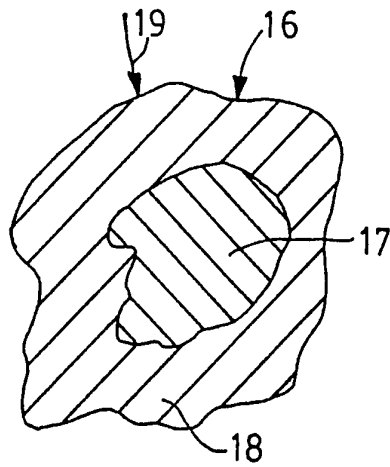


FIG-1

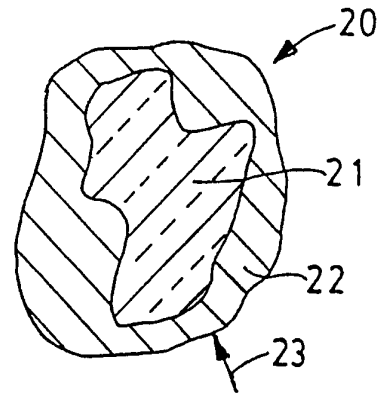


FIG-2

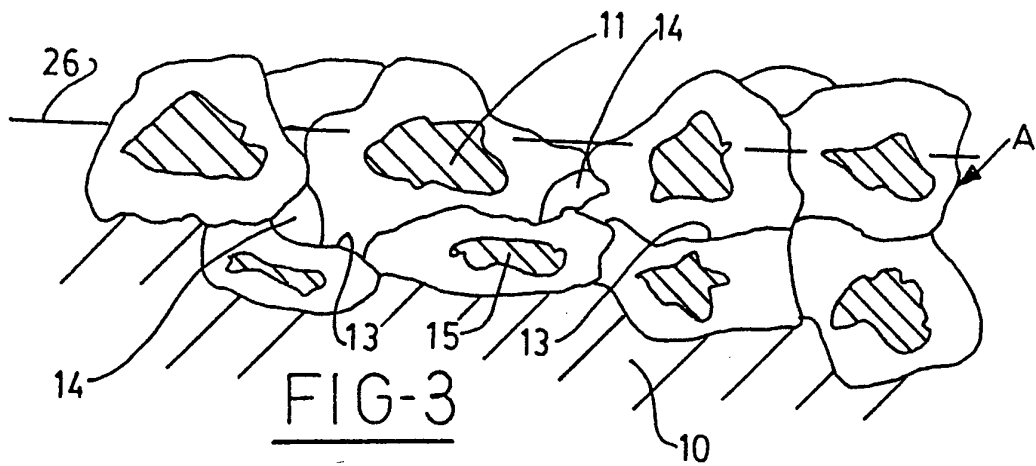


FIG-3

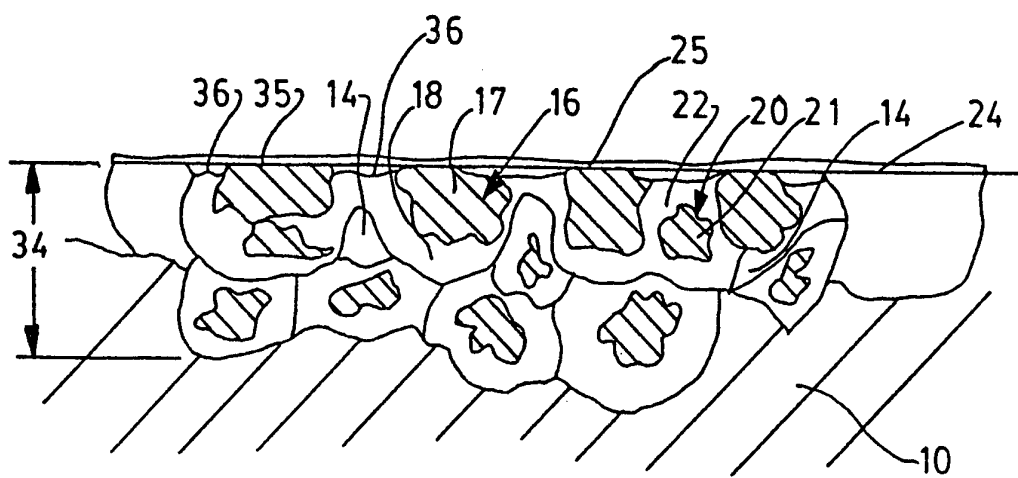


FIG-4

- 2 / 8 -

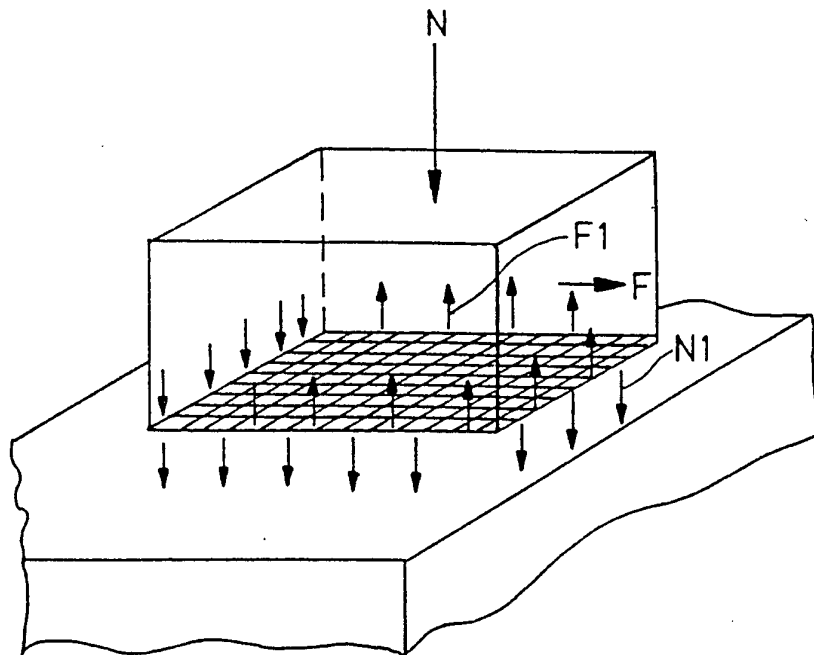


FIG-5

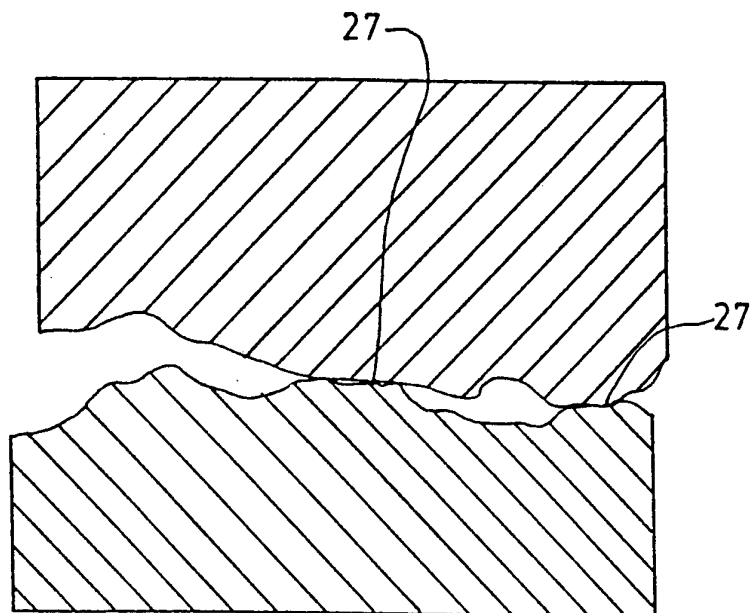


FIG-6

- 3 / 8 -

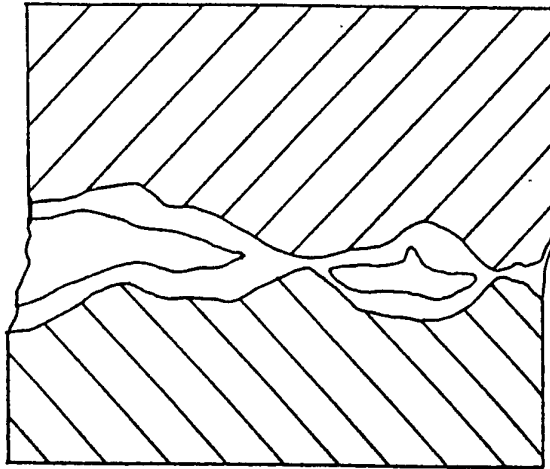


FIG-7

T_S = CRITICAL RESOLVED STRESS FOR SLIP
(ONSET OF PLASTIC FLOW)

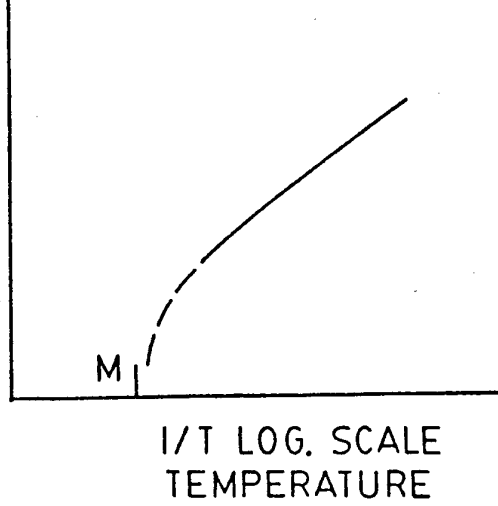


FIG-8

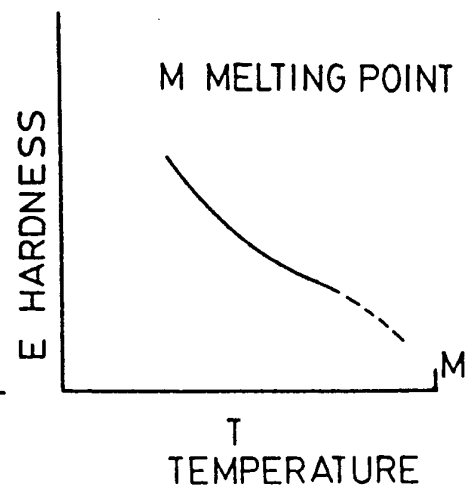
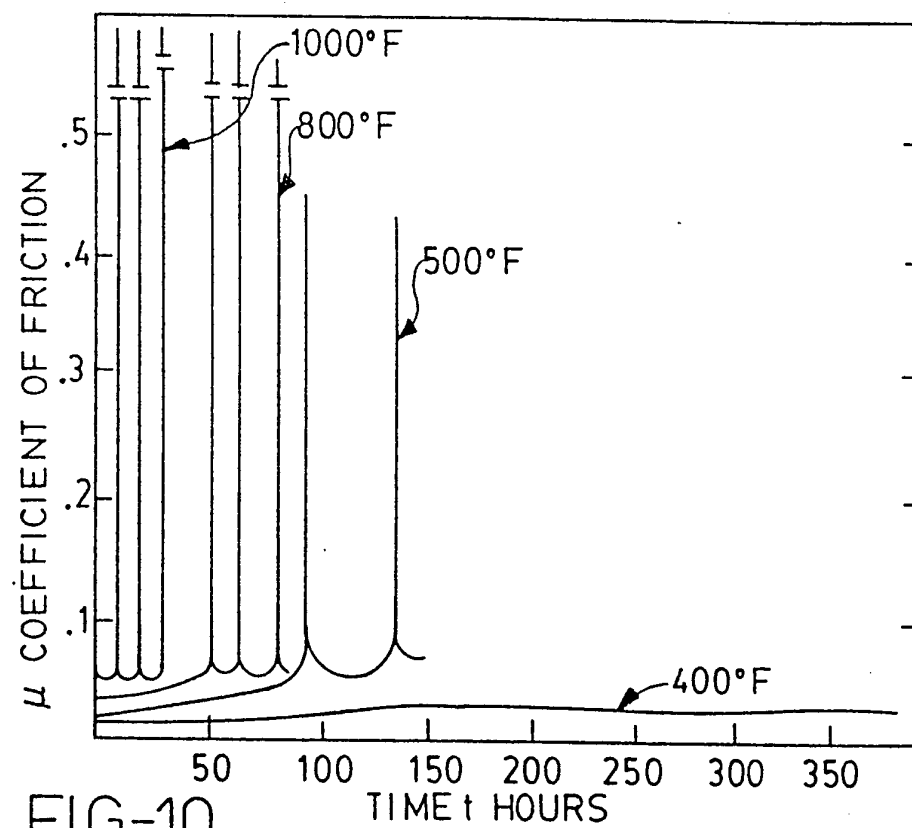
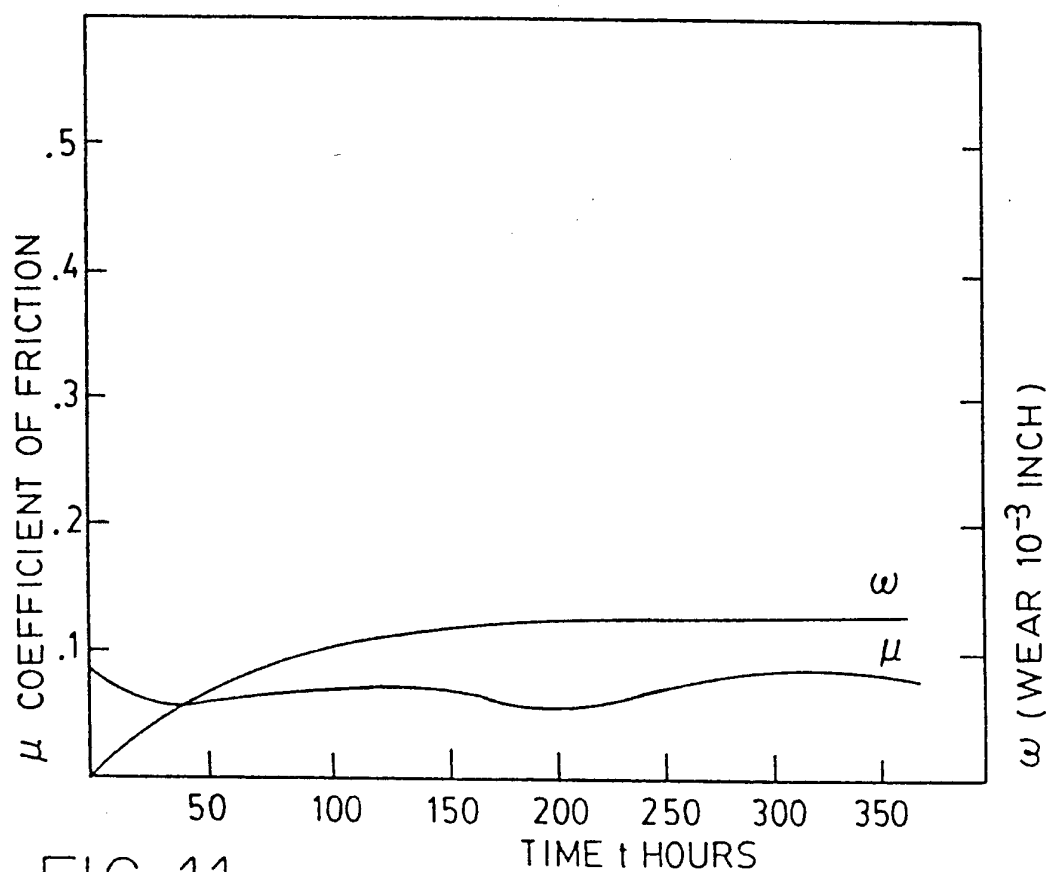


FIG-9

FIG-10FIG-11

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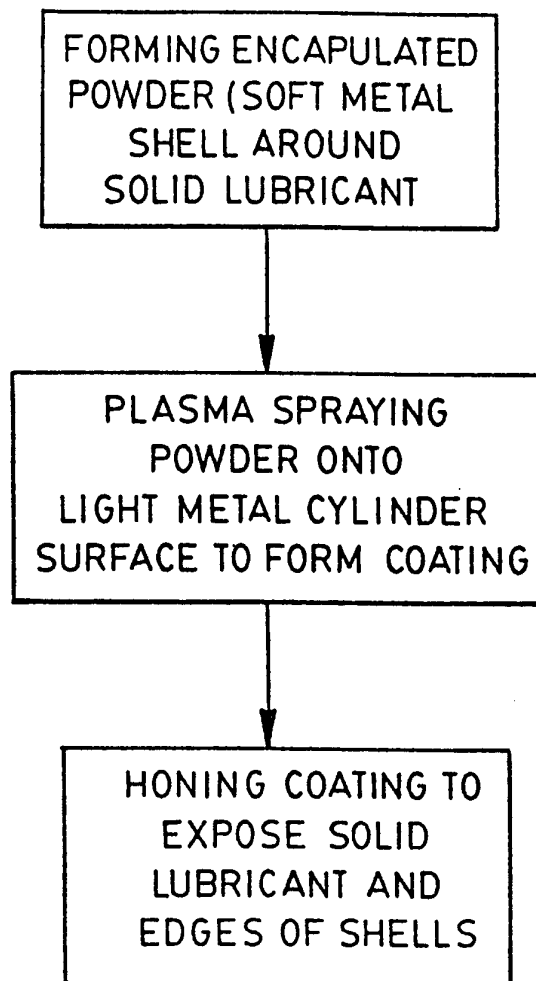
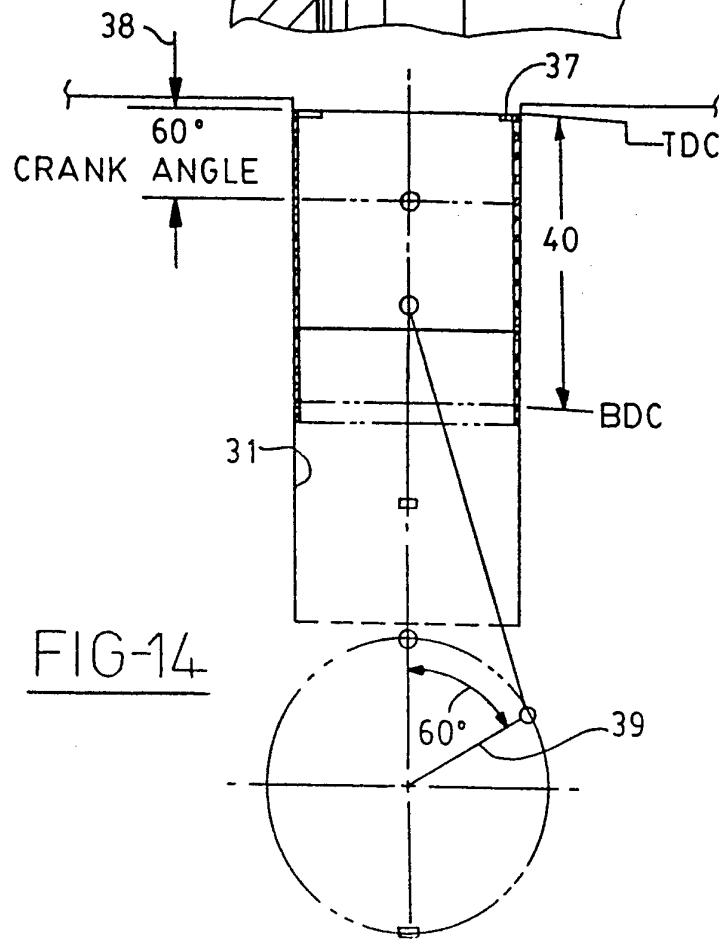
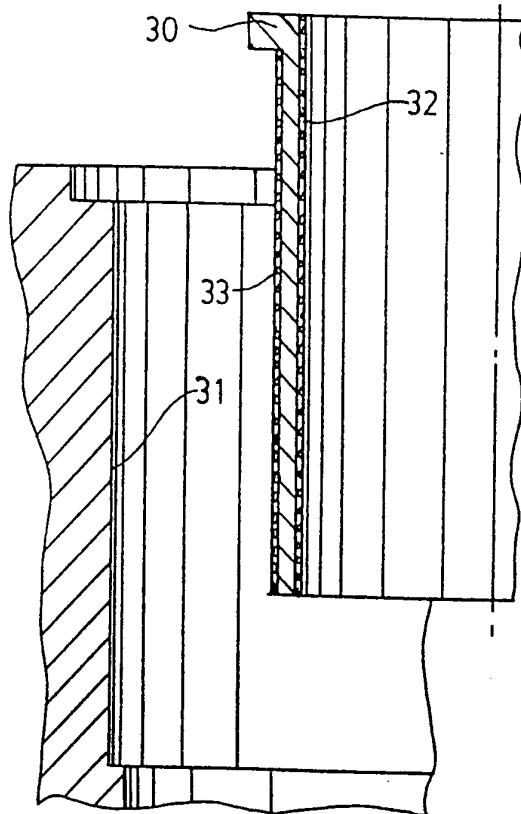


FIG-12



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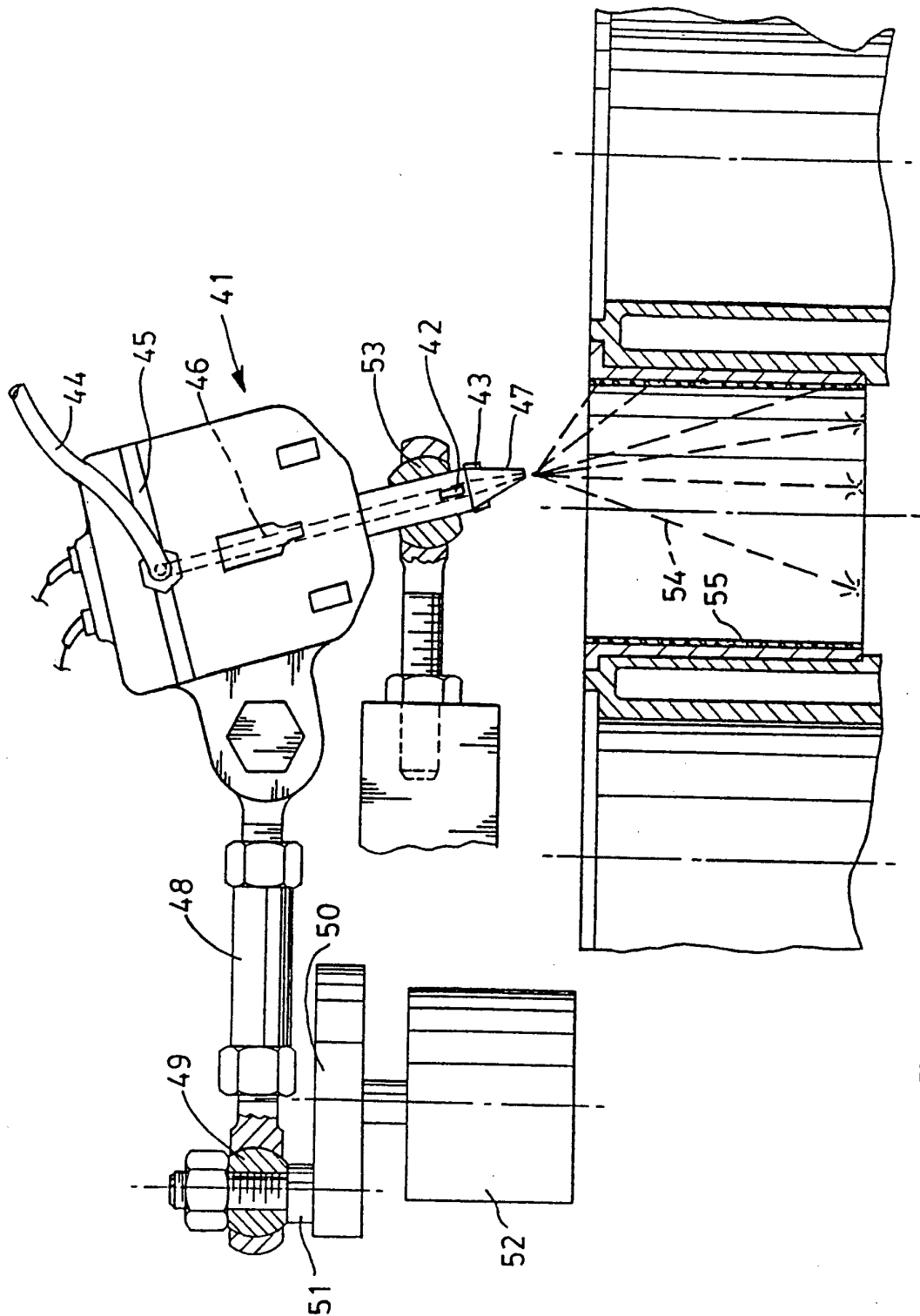
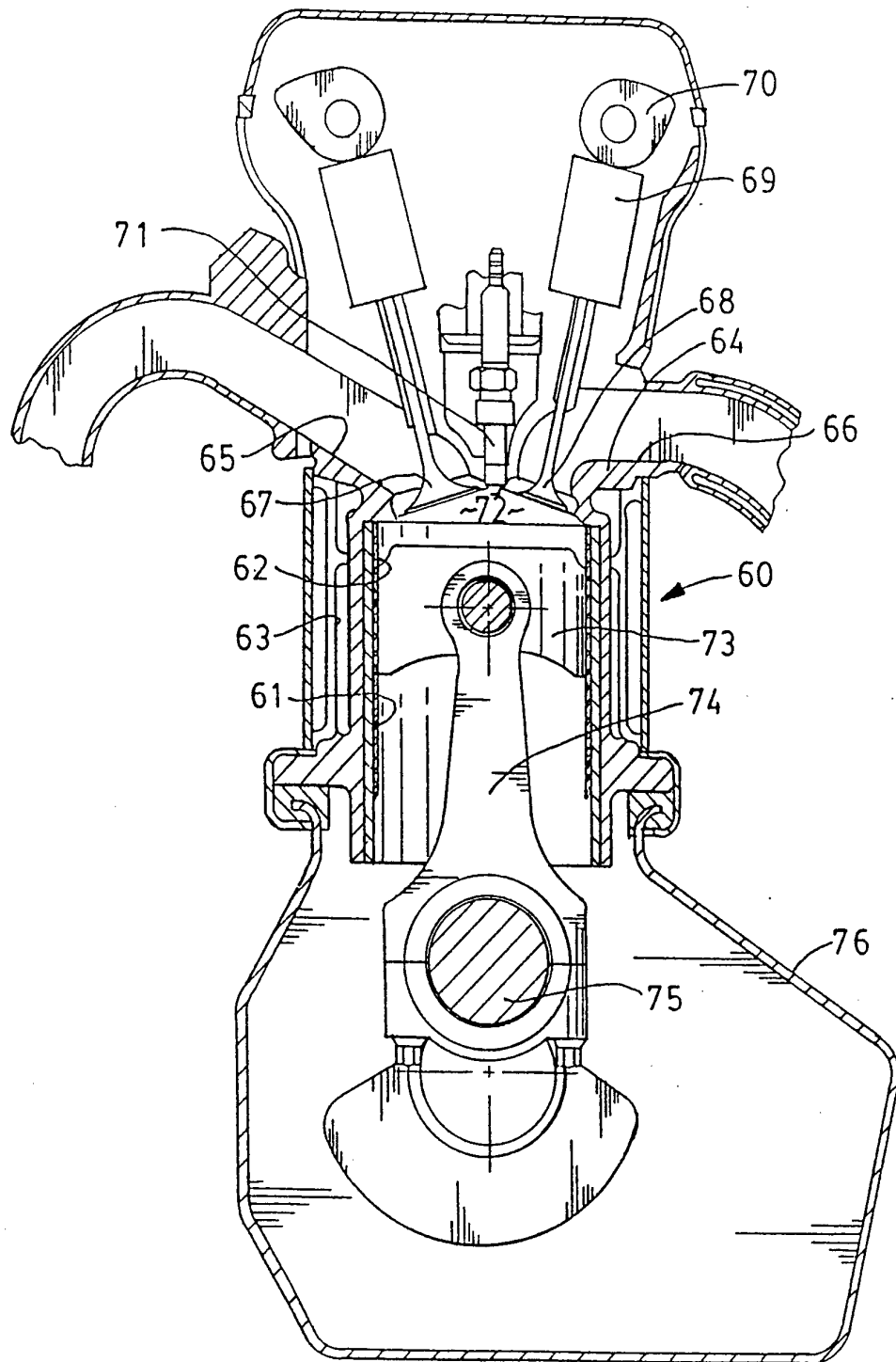


FIG-15

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FIG-16

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/GB 94/01365

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10M103/00 C10M177/00 C23C4/04 F02F1/20
/(C10M103/00, 103:02, 103:04, 103:06), C10N40:25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10M C23C F02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US,A,3 468 699 (R.D. KREMITH) 23 September 1969 see column 2, line 12 - line 13 see column 2, line 44 - line 45 see column 3, line 56 - line 58 ---	1,5 10,14, 18,21,27
X A	DE,A,17 71 640 (GOETZEWERKE FRIEDRICH GOETZE) 13 January 1972 see page 2, last paragraph - page 3, paragraph 1 see claims 1,4 --- -/--	1,5 10,14,21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "&" document member of the same patent family

Date of the actual completion of the international search

29 September 1994

Date of mailing of the international search report

12. 10. 94

Name and mailing address of the ISA

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Authorized officer

Hilgenga, K

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
PCT/GB 94/01365

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	DE,A,25 45 242 (METALLGESELLSCHAFT) 21 April 1977 see page 4, line 13 - line 18 ---	34,37,38
A	DE,A,41 33 546 (MAHLE GMBH) 15 April 1993 see claim 1 ---	34,38,40
A	US,A,4 728 448 (H.E. SLINEY) 1 March 1988 see claims 1,2 -----	

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PCT/GB 94/01365

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