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(54) **Title:** METHOD AND COMPOSITION OF MATERIALS FOR MAKING WEAR RESISTANT SURFACE COATING

(57) **Abstract:** The invention relates to a method and a composition of materials for making wear resistant surface coatings and additionally making composition of material suitable for preparing wear resistant coatings, that can be used principally for increasing the surface hardness of metals and alloys in order to enhance their wear resistance. The invention is a method for making wear resistant surface coatings, which is characterized by that, hard metal oxides, preferably Al_2O_3, Fe_2O_3, Fe_3O_4 or SiO_2, carbides, preferably SiC, Fe_3 or B_4C, nitrides, preferably cBN, CN_x, or TiN, borides, preferably FeB or TiB_2, and/or particulates of compound mixtures of said materials, preferably boron carbonitride or titanium carbonitride or silicon oxinitride and/or particulates of mixtures of said materials is provided by the incorporation of particulates comprising of different hard materials, or mixtures of particulates of said hard materials, or liquid suspensions of these particulates or mixtures of said particulates, or components of a carrier or gel-like emulsions of these particulates or components of mixtures of said particulates, or dispersed components of a solid carrier comprising of said particulates and mixtures of said particulates is attained by application to the frictioning interface of metals and alloys by pressure of preferably 400-5000 MPa that is available during either the production or the use of these metals or alloys. In some instances, the procedure is repeated with decreasing grain sizes consecutively, until the required surface roughness is achieved. The invention is further a composition of materials suitable for making wear resistant surface coating for application preferably during method according to the present invention, which is characterized by that, the composition of materials comprises oxides and/or borides and/or carbides as surface hardening materials.

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Method and composition of materials for making wear resistant surface coating

The invention relates to a method and a composition of materials for making wear resistant surface coating and additionally making composition of material suitable for preparing wear resistant coatings, that can be used principally for increasing the surface hardness of metals and alloys in order to enhance their wear resistance.

In the state of art there are different methods used for making wear resistant surface coatings. Also known a method from Hungarian Patent No. HU 196 330 which describes how to prepare wear-resistant diamond coating to the surface of metals. In the course of this process an oil-diamond suspension is coated to the surface and the suspension is incorporated into the surface by using a ram with hard metal slab (e.g. cast-iron slabs). The incorporation takes place by the high pressure produced by the hard metal slab of the ram which is kept in a rotation speed of 2-40 s^{-1}. The drawbacks of this method are: the low productivity and the high cost due to the costly diamond particulate used. This technique does not permit to coat economically large surfaces, because the incorporation of the diamond into the surface needs 20-30 minutes.

Another Hungarian Patent No. HU 198 414 presents a method for the incorporation of the diamond into the surface, where the emery containing diamond particulates is coated to the surface of the workpiece, then the total surface of the workpiece is pressed by a ram made of hard metal using 10-50 MPa pressure together with electrical pulses to enhance the incorporation of the diamond. The energy consumption of this method is high and because it needs a very expensive, high power ram with large surface and use of high-cost diamond particulate, this method is extremely expensive.

The diamond particles have a good adhesion to metal surfaces containing carbide forming elements (Fe, Ni, Si, etc.). The diamond layer, however, easily converts to graphite and loses its hardness in between 600-700 degrees Celsius in air. In the presence of carbide forming elements (Fe, Ni) this conversion to graphite can start at already 500 degrees Celsius. Because of this conversion diamond can not be used for hardening iron-containing metal surfaces, if they are subjected to extreme temperature and stress. This is the case of railway rail-wheel interface, where extreme high pressures and high peak temperatures could occur. On the other hand the high price of the diamond also limits the wide range application for these kinds of coatings.

The main disadvantages of the known methods are: the low productivity, high costs, because they apply the expensive diamond particulate for material hardening, and they also use expensive ram machines and consume valuable amount of energy during the coating. These methods can be economically used only in special cases. The known methods exclude the surface hardening of metals and alloys that are already in use as active parts of machines, e.g. the surface of laid down rails and the wheel flanges of railway carriages.

The aim of the invention is to eliminate the imperfections of the known methods, that is to develop such a process for manufacturing surfaces with hard coatings, which is capable to produce wear-, and corrosion-resistant coatings on such metal surfaces e.g. constructive parts of functioning machines, or laid-down railway rails, or wheel flanges of railway carriages, at low cost and high productivity, in order to decrease their wear rates and deterioration.

It is a further aim of the invention to accomplish the surface hardening and adjust the surface roughness by the application of less expensive, but still very hard materials oxide, carbide, boride, nitride or mixture thereof, instead of the expensive diamond particulates.

It is another further aim of the invention to use for surface hardening of metals and alloys the high pressure that is already present during the production and/or operation of metals and alloys, instead of the use of expensive ram equipment.

It is another further aim of the invention to apply particulates with decreasing grain sizes consecutively in order to enhance the incorporation of the hard particles into the surface and to improve the surface hardness, and to adjust the surface roughness.

It is another further aim of the invention to develop a method for surface hardening that applies hard particulates of oxide, carbide, boride, nitride or any compound mixture thereof, which are previously armored by such metals and/or alloys which form alloy with the base-metal to be coated, using this method after the incorporation of particulates or alloys into the surface of the base-metal the adhesion of particles armored by metals or alloys is enhanced considerably, and the hardness and wear resistance of the base-metal is increased.

It is another further aim of the invention to use particulates which are enfolded with hard carbon based coatings to enhance the adhesion and hardness thereof and simultaneously to decrease the friction coefficient of the hard coating after the incorporation to the surface of the base-metal.

It is another further aim of the invention to apply particulates consisting of different hard materials with different grain sizes, simultaneously, and by modifying the weight ratio and/or the grain size of the natural and enfolded particulates the surface hardening, the roughness and the friction coefficient of the base surface can be adjusted.

It is another further aim of the invention to apply mixture of particulates enfolded in carbon and/or armored by metals or alloys in the surface hardening method and, by modifying the weight ratio and/or the grain size of the particulates enfolded in carbon and armored by metal and/or alloy, the surface hardening, the roughness and the friction coefficient of the base surface can be adjusted.

It is another further aim of the invention to apply water-based emulsion containing mixtures of original particulates and those armored by metal and/or alloy and/or enfolded in carbon, with water and at least one surfactant.

It is another further aim of the invention to apply oil-based emulsion containing mixtures of original particulates and those armored by metal and/or alloy and/or enfolded in carbon mixed with oil and at least one emulsion agent.

It is another further aim of the invention to make mixtures of original particulates and those armored by metal and/or alloy and/or enfolded in carbon all dispersed in ice as solid carrier and apply to the surface.

It is another further aim of the invention to make mixtures of original particulates and those armored by metal and/or alloy and/or enfolded in carbon, all dispersed in solid, inorganic lubricant as solid carrier and apply to the surface.

It is another further aim of the invention to make mixtures of original particulates and those armored by metal and/or alloy and/or enfolded in carbon, all dispersed in solid, organic lubricant as solid carrier and apply to the surface.

It is another further aim of the invention to make mixtures of original particulates and those armored by metal and/or alloy and/or enfolded in carbon, all dispersed in solid mixture of organic and inorganic lubricants as solid carriers and apply to the surface.

It is another further aim of the invention to develop such composition of materials, that can be advantageously, simply and economically applied for increasing the surface hardness of metals and alloys and decreasing the friction coefficient and corrosion.

When working out the solution according to the invention we realised that the set tasks can be easily completed if we replace the expensive diamond particulate by less expensive, but still very hard particulates of oxide, carbide, boride, nitride or compound mixture thereof, and apply them for surface hardening such a way that those particulates are dispersed to the surface to be hardened by dry scattering, or spraying of their emulsions formed in liquids or anointing their dispersion with greases or solid carriers, and instead of the use of expensive ram machines for incorporation of the grains we apply the high pressure that is already present during the production and/or operation of metals and/or alloys.

We realised that it is beneficial if we apply particulates with decreasing grain sizes consecutively, so we can improve the incorporation of the hard particles into the surface and increase the surface hardness, and adjust the surface roughness, and in order to enhance the adhesion of hard particulates, it is also beneficial to deposit onto the surface of particulates in advance a layer of metal, or diamond, or Diamond Like Carbon (DLC) the latter is being a mixture of graphite and amorphous carbon, those layers after alloying with the base-metal or compounding with it in a carbide form, they can effectively enhance the adhesion of hard particulates to the surface of the base-metal or alloy, and they do not lose their hardness at stresses due to high temperature and pressure. Examples for such particulates are listed in Table 1.

The invention is a method for making wear resistant surface coating, which is characterized by that,
- incorporation of particulates to the surface of metals
-hard metal oxides, preferably Al(2)O(3), Fe(2)O(3), Fe(3)O(4) or SiO(2),
-carbides, preferably SiC, Fe(3)C vagy B(4)C,
-nitrides, preferably cBN, CN(x) or TiN,
-borides, preferably FeB or TiB(2)
and/or particulates of compound mixtures of said materials, preferably boron-carbo-nitride or titanium-carbo-nitride or silicon-oxi-nitride and/or particulates of mixtures of said materials is provided by the incorporation of
-particulates comprising of different hard materials,
-or mixtures of particulates of said hard materials,
-or liquid suspensions of these particulates or mixtures of said particulates ,
-or components of a carrier of gel-like emulsion of these particulates or components of mixtures of said particulates,
-or dispersed components of a solid carrier comprising of said particulates and mixtures of said particulates
is attained by application to the frictioning interface of metals and alloys by pressure of preferably 400-5000 MPa that is available during either the production or the use of these metals or alloys and in some instances, the procedure is repeated with decreasing grain sizes consecutively, until the required surface roughness is achieved.

In one of the preferred applications of the method according to the invention the surface of said hard oxides, carbides, nitrides or borides and mixtures of said materials is coated with a layer of metal or alloy, which builds alloy with the material of the surface to be coated.

In another preferred application of the method according to the invention on the surface of the grains of said particulates enfolded with a hard carbon-base coating layer of DLC and/or amorphous carbon is made by a mechanical, thermal or other method: such as e.g. pyrolysis, CVD or plasma deposition.

In a further preferred application of the method according to the invention hard grains of different particle size and materials are used in said particulates in the same time and surface hardness, roughness and friction coefficient of the metals and alloys is set by changing the weight ratio or grain size of natural and/or armored and/or enfolded particulates.

In a further preferred application of the method according to the invention in said particulates the carbon-base enfolded particulates are in 3-80 weight percent, the metal or alloy-base armored particulates are in 20-97 weight percent applied together and the value of surface hardness, roughness and friction coefficient is set by the weight ratio of carbon-base enfolded and/or metal or alloy-base armored particulates and/or the weight ratio of materials of different grain size.

In a further preferred application of the method according to the invention during the method certain different grain size surface-hardening fractions are applied consecutively, in given case during several cycles applying decreasing grain sizes and the surface roughness is set this way.

In a further preferred application of the method according to the invention during the method several surface hardening materials of different grain size are applied, and they are embedded in the surface in a single cycle.

In a further preferred application of the method according to the invention said liquid comprises of water and at least one dispersion agent and it is applied to the surface by spraying or vaporization.

In a further preferred application of the method according to the invention said liquid comprises of oil or at least one type of dispersion agent and it is applied to the surface by spraying or vaporization.

In a further preferred application of the method according to the invention said liquid comprises of oil, water and at least one type of emulsion agent and dispersion agent and it is applied to the surface by spraying or vaporization.

In a further preferred application of the method according to the invention the mixture of hard natural particulates, enfolded and armored particulates is applied to the surface to be treated by lubrication as gel-like emulsion.

In a further preferred application of the method according to the invention said solid carrier comprises of ice and is applied to the surface by greasing and/or melting.

In a further preferred application of the method according to the invention the carrier contains inorganic lubricants, such as e.g. graphite, MoS(2), Cu respectively mixtures of said materials.

In a further preferred application of the method according to the invention organic lubricants, such as e.g. PTFE (polytetrafluorethylene), polyethylene, polyamide, paraffin, stearin, respectively mixtures of said materials are used as carriers.

In a further preferred application of the method according to the invention solid organic lubricants, such as e.g. polyethylene, polyamide, paraffin, stearin, and solid inorganic lubricants, such as e.g. graphite, MoS(2), Cu are used together as carriers.

In a further preferred application of the method according to the invention the carrier comprises of 1-30 weight percent dispersed particulates, 1-10 weight percent friction reducer organic and inorganic lubricants and 40-98 weight percent organic lubricant.

The invention is further a composition of materials suitable for making wear resistant surface coating for application preferably during method according to the present invention, which is characterized by that, the composition of materials comprises oxides and/or borides and/or nitrides and/or carbides as surface hardening materials.

In one of the preferred embodiments of the composition according to the invention the surface hardening material is:

- natural particulates (grains of their own) or mixture of particulates, and/or
- particulates, which are armored with metal or alloy coating and/or
- particulates, which are enfolded with carbon based coatings (DLC –diamond-like hard carbon coating and mixture of amorphous carbon and graphite) or mixture of said materials.

In another preferred embodiment of the composition according to the invention the surface hardening materials, particulates are preferably
- hard particulate oxides, which are the mixtures of metals in columns 4b, 5b, 6b of the periodic table, as well as compounds of Al, Si and Fe with elements B, C, O, N and mixtures of said particulates, moreover mixture compounds of said elements and materials containing in given case solid lubricant, reducing friction.

In a further preferred embodiment of the composition according to the invention the surface hardening material comprises preferably oxides, such as aluminum oxide (Al(2)O(3)), iron oxide (III) (Fe(2)O(3)), iron oxide (Fe(3)O(4)), titanium dioxide (TiO(2)),or silicon-dioxide (SiO(2)), magnesium oxide (MgO), or other hard oxides,
carbides, such as silicon carbide (SiC), iron carbide (Fe(3)C), tungsten carbide (WC), or boron carbide (B(4)C), or other hard carbides,
nitrides, such as boron nitride (cBN), or carbo nitride (CN(x)) or titanium nitride (TiN), silicon nitride (Si(3)N(4)), aluminum nitride (AlN), titanium nitride (TiN), tantalum nitride (TaN), iron nitride (FeN), molybdenum nitride (MoN), tungsten nitride (WN), or other hard nitrides,

borides, such as iron boride (FeB), titanium-diboride (TiB(2), aluminium-diboride (AlB(2)), chromium boride (CrB(2)), zirconium-boride (ZrB(2), or other hard borides, or mixtures of these materials, such as boron carbo nitride (cBC(2)N), titanium carbonitride (TiCN) or silicon oxi-nitride (SiON), aluminium titanium oxide (Al(x)Ti(y)O(z)), or other hard mixtures of compounds, respectively and mixtures of these materials.

In a further preferred embodiment of the composition according to the invention the grain size of the particulates in the material applied for surface hardening is in 1 mm-2nm range.

In a further preferred embodiment of the composition according to the invention the hard particulate is dispersed in liquid suspension, said liquid suspension carrier comprises of

- preferably water and surfactant and dispersing agent,
- mineral-, and/or vegetable-, and or synthetic-oil and emulsion agent, or
- water, and/or mineral, and/or vegetable-, and/or animal- and/or synthetic-oil and emulsion agent,

furthermore in given case anticorrosion agent.

In a further preferred embodiment of the composition according to the invention in a preferred embodiment the composition of materials comprises of 1-30 weight percent hard particulates dispersed in liquid, 55-98 weight percent liquid carrier, 1-10 weight percent solid friction reducing lubricant and 0.1-5 weight percent corrosion inhibitor.

In a further preferred embodiment of the composition according to the invention the surface hardening material consisting of hard particulates is dispersed in a gel-like material, which carrier in given case consists of

-vegetable and/or animal-, and/or mineral, and/or synthetic oil, or
-palmitic and stearic acid mixture, or
-mixture of oil and solid paraffin, or
-mixture of solid paraffin, stearic acid and oil, furthermore in given case corrosion inhibitor.

In a further preferred embodiment of the composition according to the invention in a preferred embodiment the gel-like material consists of 1-30 weight percent hard particulate dispersed in grease, 55-98 weight percent grease carrier, 1-10 weight percent solid friction reducing lubricant as well as 0.1-5 weight percent corrosion inhibitor.

In a further preferred embodiment of the composition according to the invention the surface hardening material comprising of hard particulates is dispersed in a solid carrier, and said solid carrier consists of:

- ice, or
- paraffin, stearic acid and mixture thereof and surfactant, or
- plastics, such as polyamide (Nylon), polyethylene (PE), polytetrafluorethylene (PTFE) or other plastics with low friction coefficient,

furthermore in given case friction reducer and/or corrosion inhibitor.

In a further preferred embodiment of the composition according to the invention (in a preferred embodiment) the composition consists of hard particulate dispersed in solid carrier by 1-30 weight percent, solid carrier by 55-98 weight percent, solid friction reducing lubricant by 1-10 weight percent, furthermore corrosion inhibitor by 0.1-5 weight percent.

In a further preferred embodiment of the composition according to the invention the composition consists of hard particulates that have previously been enfolded in hard carbon coating (DLC, mixture of graphite and amorphous carbon) to reduce friction, furthermore solid lubricants (graphite, PTFE, iron oxides, MoS(2), TiO(2), hexagonal boron nitride) are added to further decrease friction coefficient.

Preferred applications of the method according to the invention are set forth by the following description as follows:

In a preferred application of the method according to the invention, the abovementioned set tasks were solved according to the invention so, that we replaced the expensive diamond particulates by less expensive, but still very hard particulates of oxides, such as Al(2)O(3), Fe(2)O(3), Fe(3)O(4) or SiO(2), carbides, such as SiC, Fe(3)C or B(4)C, nitrides such as cBN, CN(x) or TiN, borides such as TiB(2) or compound mixtures thereof, such as titanium carbo-nitride or silicon oxi-nitride and applied them for surface hardening such a way that those particulates were dispersed to the surface to be hardened by dry scattering, or spraying of their emulsions formed in liquids or anointing their dispersion with greases or solid carriers, and instead of using expensive ram machines for incorporation of the grains we applied the high pressure (400-5000 GPa) already present during the production and/or use of metals and/or alloys and we repeated the process applying particulates with decreasing grain sizes consecutively, until the required surface roughness was achieved.

This technique is more economical to use, due to application of less expensive, hard particulates as well as exploitation of the extreme high pressure of 400-5000 GPa available during production or use of metals than known methods in the art. Hardness of surfaces treated such a way increases considerably, surface roughness decreases, so it becomes more wear resistant. Particulates in the coating resist well chemical affects, such as oxidation, so the coating decreases corrosion of the base-metal as well.

Embedding of particulates into the metal surface results in surface hardening due to various effects:

The primary cause of hardening is the high temperature and high pressure resulting from the high pressure used during incorporation when metal melts locally and reacts with the grains of the particulates and produces a metal-ceramic composite having characteristics of both metals and alloys as well as ceramics, i.e. ductility and excellent wear- and corrosion resistance.

The secondary cause of hardening is the fact, that penetrating particulates compact the original crystal grains of the metal and create a high compressive mechanical stress on the surface.

The tertiary cause of hardening is, that during incorporation of particulates the formation of number of crystal defects, dislocations occur resulting in increase of hardness similarly to forging (microforging).

The highest proportion of increase of hardness is due to creation of composites. Hardness of the hard layer in case of a one-component particulate can be calculated approximately as follows:

$$HR = HV(1) \times (1-K) + HV(2) \times K$$

where is:

HR	- Vickers hardness of the coating
HV(1)	- Vickers hardness of the base-metal
HV(2)	- Vickers hardness of the hard particulate
K	- volume proportion of the hard particulate in the layer

The method according to the invention from this respect is the mixture of making a metal-ceramic composite in-situ and that of a micro-forging process. The composite made at low temperature, and the surface coating compacted by micro-forging, possessing compressive stress as well as the crystal dislocations in the base-metal, all considerably increase the wear and corrosion resistance of the metal and at the same time the metal retains its ductility as well.

In a further preferred application of the method according to the invention, hardening of the surface can be further enhanced if such very hard oxides as Al(2)O(3)), Fe(2)O(3), Fe(3)O(4) or SiO(2), carbides as SiC, Fe(3)C or B(4)C, nitrides as cBN, CN(x) or TiN, borides as TiB(2) or compound mixtures thereof such as titanium carbo nitride or silicon oxi nitride are used, which are previously armored by such metals and/or alloys which form alloy with the base-metal to be coated, using physical, chemical, electrochemical or plasma methods such as e.g. metal spraying or electroplating, or CVD plasma deposition, and the grains of the mentioned particulates or the mixtures thereof are incorporated into the surface of the base-metal using the high surface pressure available during either the production or in he course of the use of these metals.

In such a way, that the abovementioned armored particulates or mixtures thereof are embedded in the surface by scattering, or spraying the liquid base suspension of these particulates and/or their mixtures, by smearing the solid carrier dispersed by these particulates and/or their mixture to the frictioning interface of metal surfaces, and the grains of the mentioned particulates are incorporated into the surface of metals and alloys applying high pressure, that is available during either the production or the use of these metals and alloys and the procedure is repeated with decreasing grain sizes consecutively, until the required surface roughness is achieved.

In this way the coating of the metal can be carried out at a considerably lower 250-1500 MPa surface pressure as well. The metal used for armoring particulate is capable of building alloy with the base-metal during embedding particulates due to the increase in temperature caused by friction, as well as due to its high solubility in the base metal, and it is capable of forming an alloy with the base-metal at lower pressures and so it joins hard particulate and the base-metal by strong metallic bond. With the use of armored hard particulates, which has metal coating on the surface that easily alloy with the base-metal even at low temperature and pressure, the resulting hard coating has especially good bonding strength, great hardness, wear-, and corrosion resistance properties in case of lower embedding pressure as well.

In a further preferred application of the method according to the invention, where suitable hard surface coating is made by applying such grains of very hard oxides as Al(2)O(3)), Fe(2)O(3), Fe(3)O(4) or SiO(2), carbides as SiC, Fe(3)C or B(4)C, nitrides as cBN, CN(x) or TiN, borides as TiB(2) or mixtures thereof such as titanium carbo-nitride or silicon oxi-nitride which are previously enfolded by hard carbon based coating using physical, chemical, electrochemical or plasma methods such as e.g. metal spraying or electroplating, or CVD plasma deposition, and the grains of the mentioned particulates or the mixtures thereof are incorporated into the surface of the base metal using the high surface pressure available during either the production or the use of these metals, such a way that those carbon enfolded particulates or mixtures thereof are dispersed to the surface by dry scattering, or spraying of their suspensions formed in liquids or anointing their dispersion with greases or solid carriers, to the frictioning interface of metal surfaces and the high pressure already present during the production and/or use of metals and/or alloys is applied to incorporate them and the process applying particulates with decreasing grain sizes is repeated consecutively, until the required surface roughness is achieved.

Very hard carbon-base coating layers can be made by mechanical, thermal or chemical (CVD) methods on the surface of the hard particulates. These carbon-based layers mostly consist of diamond-like carbon called DLC and amorphous carbon. These grains are of extraordinary hardness, low friction coefficient, therefore their wear resistance is excellent. Particulates, which are enfolded with carbon based coatings can be very easily embedded in metals and alloys at quite low pressure as well. Due to their extraordinary hardness and low friction coefficient wear resistance of metals and alloys treated by them is enhanced to a great extent.

Particulates, which are enfolded with carbon based coatings can be very easily embedded in metals and alloys particularly to the surface of carbide forming elements and alloys, such as base-metals and alloys with e.g. iron, nickel, cobalt, titanium and molybdenum content. The friction coefficient of such embedded surfaces is considerably lower, than that of natural particulates, therefore the friction coefficient of the treated surfaces can be adjusted in a wide range by changing the weight ratio of enfolded and natural particulates.

The speed of forming hard coating on basis of the method according to the invention, has considerably increased compared to methods in the state of art, whereas the costs of forming the coating has considerably decreased resulting from the application of less expensive hard oxides, carbides, nitrides, borides or mixtures thereof. The abovementioned particulates have good corrosion resistance protecting thereby the metal below from corrosion. As embedding of particulates into the surface takes place continuously during production and/or use of metals and alloys, productivity of forming hard surface coating has been increased by 100-1000 times compared to the method in the state of art.

In a further preferred application of the method according to the invention, it is beneficial to use such a metal-hardening method, which applies such mixture of oxides, for making hard coating on metal surfaces as aluminum oxide (Al(2)O(3), (Fe(2)O(3), (Fe(3)O(4), or (SiO(2), or carbides, such as (SiC), (Fe(3)C), or (B(4)C), or nitrides, such as (cBN), (CN(x) or borides, such as (TiB(2), or compound mixtures of these materials, such as titanium carbo-nitride or silicon oxi-nitride representing hard grains of different particle size and different materials used in the particulates in the same time and the required friction coefficient is set by the weight ratio of natural particulates and metal armored and/or carbon enfolded particulates, whereas grain size of natural and enfolded and/or armored particulates regulates surface roughness.

Particulate mixture is applied by dry scattering, or spraying of their suspension formed in liquids or anointing their dispersion with greases or solid carriers, to the frictioning interface of metal surfaces, and the grains of the mentioned particulates are incorporated into the surface of metals or alloys applying high pressure, that is available during either the production or the use of these metals or alloys.

A hard coating formed this way ensures, that an extremely hard, still elastic layer is formed on the surface of metals and alloys resulting in significant decrease of wear and improvement of corrosion resistance of metals and alloys, and surface hardness, and friction coefficient between metals and alloys can be set by changing the weight ratio of natural and/or enfolded and/or armored particulates whereas surface roughness can be independently adjusted in a wide range by choosing the grain size of natural and enfolded or armored particulates. Grain size to be applied is preferably in range of 1 mm- 2 nm. In case of steel grain size is preferably within the range of 20 micrometer – 2 nm.

Physical properties of certain particulates can be calculated by the method of effective-medium approximation, i.e. by weighting of their volume proportion to realize changing of physical properties.

In a further preferred application of the method according to the invention, with mixing the grains of the particulates and previously enfolded particulates of the abovementioned hard oxide or carbide or nitride or boride or mixture thereof in such a way, that 3-80% of carbon enfolded particulates, 20-97% of metal or alloy armored particulates are applied together and the required surface hardness, friction coefficient and surface roughness can be achieved by adjusting the weight ratio and grain size of the particulates.

Particulate mixture is applied by dry scattering, or spraying of their suspension formed in liquids or anointing their dispersion with greases or solid carriers, and applying them to the frictioning interface of metal surfaces, and the grains of the mentioned particulates are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys.

Surface coating formed this way has extremely good bonding strength, great hardness, whereas surface roughness is low, resulting in a dramatic decrease of surface wear and considerable improvement of corrosion resistance and simultaneously the friction between metals and alloys can be adjusted to the required value.

In a further preferred application of the method according to the invention, it is beneficial to apply the mixture of hard natural and enfolded and/or armored particulates to the surface in such a way, that with the help of dispersion agent or agents and with water a dispersion is made and it is sprayed onto the metal surface. Water dispersion is preferable, because it does not involve environmental pollution. After incorporation of hard particulates water can ensure cooling and lubricating of the surface as well.

In a further preferred application of the method according to the invention, it is preferable using such a method for hardening the metal and alloy surfaces which provides embedding of hard particulates or mixtures thereof into the surface by using their a suspension with dispersion agent and oil. This suspension is applied onto the surface of the frictioning interface of metal surfaces, and the grains are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys. After incorporation of hard particulates the oil film left on the metal surface would decrease friction. Therefore this suspension can ensure good wear resistance for the hardened surface metal.

In a further preferred application of the method according to the invention, it is preferable using such a method for hardening the metal and alloy surfaces which provides embedding of hard particulates or mixtures thereof into the surface by using their dispersion in emulsion of water and oil. This emulsion is applied onto the surface of the frictioning interface of metal surfaces, and the grains are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys. Embedding takes place in a way, that the abovementioned liquid consists of oil, water and at least one type of emulsion agent and dispersion additive.

Hard particulates can be produced on basis of the periodic table by CRC Handbook of Chemistry 48th Edition, compounds of elements of columns 4b, 5b, 6b i.e. aluminium, silicon, iron with elements appearing in columns 3a, 4a, 5a.

In a further preferred application of the method according to the invention, it is preferable using such a solution for hardening the metal and alloy surfaces which provides embedding of hard particulates or mixtures thereof into the surface by using a gel-like emulsion of water, emulsion agent viscosity enhancer and dispersion agent which is applied onto the surface of the frictioning interface of metal surfaces, by greasing. Application of a gel-like (semi-rigid) paste-like material is preferable, as it does not involve environmental pollution and it can be applied locally as greasing material e.g. as lubricating grease. After incorporation of hard particulates onto the surface lubricant can ensure cooling and greasing of the surface, moreover it decreases friction as well.

In a further preferred application of the method according to the invention, with applying the grains of the particulate and previously enfolded and/or armored particulates of the abovementioned hard oxide or carbide or nitride or boride or mixture thereof in a solid carrier dispersed in ice. The solid lubricant is applied onto the surface of the frictioning interface of metal surfaces by greasing, and the grains are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys.

This way the particulates applied to the surface with ice, as a lubricant, can be incorporated in the metal or alloy surfaces with especially strong bond resulting from expansion of ice after warming up during embedding. Ice as a lubricant has very low friction coefficient resulting in continuous greasing without significant energy loss. Ice as carrier is preferable as well, since it does not cause any environmental harm as lubricant after melting.

In a further preferred application of the method according to the invention, it is preferable using such a solution for hardening the metal and alloy surfaces which provides embedding of hard particulates or mixtures thereof into the surface by using hard particulates or mixture thereof dispersed in a solid carrier comprising inorganic solid lubricants, such as e.g. graphite, MoS(2), Cu, respectively mixtures thereof. This solid carrier with dispersed grains is applied onto the surface of the frictioning interface of metal surfaces, and the grains are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys.

On the hardened surface produced this way the solid carrier left on the surface after the incorporation of grains provides very good friction reducing effect. The metal surface treated this way has excellent wear resistance properties resulting from metal hardening and decrease of friction even in case of enormous surface pressure.

In a further preferred application of the method according to the invention, it is preferable using such a solution for hardening the metal and alloy surfaces which provides embedding of hard particulates or mixtures thereof into the surface dispersed in a solid carrier. The solid carrier comprises organic-base solid lubricants, such as e.g. PTFE (polytetrafluorethylene), polyethylene, polyamide, paraffin, stearin, respectively mixtures of said materials. This solid carrier with dispersed grains is applied onto the surface of the frictioning interface of metal surfaces, and the grains are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys. After incorporation of hard particulates onto the surface the solid lubricant can ensure reducing friction as well. A great advantage of organic lubricants is that due to their low melting point solid dispersion can be easily prepared.

In a further preferred application of the method according to the invention, it is preferable using such a solution for hardening the metal and alloy surfaces which provides embedding of hard particulates or mixtures thereof into the surface by using hard particulates or mixture thereof dispersed in a solid carrier. The solid carrier comprises organic-base solid lubricants, such as e.g.
polyethylene, polyamide, paraffin, stearin, and inorganic-base solid lubricants, such as graphite, $MoS(2)$, Cu together. This solid carrier with dispersed grains is applied onto the surface of the frictioning interface of metal surfaces, and the grains are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys. After incorporation of hard particulates onto the surface the solid lubricant left on the surface can ensure for a long time a low friction coefficient reducing wear of carrier metal to a great extent.

In a further preferred application of the method according to the invention, with applying the metal armored and/or carbon enfolded particulates of the abovementioned hard oxide or carbide or nitride or boride or mixture thereof in a solid carrier with low friction coefficient in dispersed form as solid lubricant by greasing onto the surface of the frictioning interface of metal surfaces by greasing, and the grains are incorporated into the surface of metals or alloys applying high surface pressure, that is available during either the production or the use of these metals or alloys. The hard particulate mixture dispersed in solid carrier consisting of 1-20 weight percent of hard natural and/or enfolded and/or armored particulate mixture and 80-99 weight percent of friction reducing solid carrier has lasting effect.

Possible variations of composition of materials according to the invention is set forth in Table I attached.

The solution according to the invention is described as set forth in the examples below.

Coatings combining ductility of metals and alloys as well as stiffness and wear resistance respectively corrosion resistance of ceramics are possible to produce by the method according to the invention.

Example 1

Natural SiC particulates were scattered to harden the surface of a material of 228 HV hardness. The particulates were embedded into the surface by 1.25 GPa pressure. The hardness of the composite can be calculated by effective-medium approximation from the hardness values of component. In this example components are taken into consideration with weight corresponding to their volume concentration.

The hardness of steel was 228 HV before hardening and it increased to 268 HV after the process. Hardness of SiC was 2500 HV.

$228 \times (1\text{-K}) + 2500\text{K}=268$ solution of equation K=0.0175.

1.75% SiC embedding into the steel caused 17.5% surface hardening.

Example 2

High-speed steel needles of 2 mm diameter were hardened with SiC of 1000 fineness, Al(2)O(3) of 3 micron particle size armored with iron, SiC particulates of 1000 fineness armored with Al and Cu applying 2 GPa pressure. Friction coefficient was measured on hardened steel with 450 g load (1.43 MPa) on a Pin on Disk equipment.

	Original steel	1000 SiC coating	Al(2)O(3)+ Fe Armored coating	1000 SiC +Al Armored coating	1000 SiC+Cu Armored coating
Friction coeffi-cient t=450g	0,15	0,25	0,2	0,25	0,12
Friction coeffi-cient t=450g After 5 min.	0,15	0,30	0,45	0,38	0,15

The initial friction coefficient of the hardened metal was increased by 66% in case of 1000 SiC respectively (1000 SiC+Al) as well. After initial wear friction coefficient increased by nearly 100% in case of most armored samples. In case of (1000 SiC+Al) and (Al(2)O(3)+

Fe) of 3 micrometer grain size the friction coefficient increased by 2.5 – 3 times. In case of SiC particulate armored by Cu initial friction coefficient decreased by 20%, then after wear of the layer it got back to the original value.

Friction coefficient could be set in a wide range with mixing of various particulates. In order to set the desired friction coefficient effective-medium approximation could be used, likewise when calculating hardness.

Example 3

Natural dry 1000 SiC particulate was scattered on a stainless steel plate of 0.5 mm thickness and by dropping a body of 0.6 kg from 20 cm the particulates were embedded into a surface of 3.5 mm diameter, repeating the process 60 times. The total hardened surface was 6 cm^2. After embedding the sample was cleaned by ultrasonic shaking in distilled water, then dried and the imperfectly embedded particulates were removed by Scotch-tape breaking test.

Mass of sample after hardening	5.06350 g
Original mass	-5.06315g
	0.00035 g excess weight

Well-bonded particulates of 4-8μm could be noticed on the surface in microscope by 500 magnification.

$$3.5\ 10^{-4}\ g=3.27\ g/cm^3 \times 0.0000178cm \times 6\ cm^2,$$

which corresponded with a SiC coating of 0.178 μm average thickness.
Hardness of stainless steel before coating was: 34 HV, after coating it increased to 80 HV.

According to equation 34 x (1-K) + 2500K=80 K= 0.018, so 1.8% SiC content was embedded in the layer. The thickness of the hardened layer was 10 μm from the depth of indentation used at measuring hardening according to Vickers. SiC content of 1.8% calculated from hardness equation and that of 1.78% of weight measurement are quite close values. After hardening the steel hardness increased to more than 2.5 times to the original value, which also corresponds quite well with the hardness determined by weight measuring of the composite.

Example 4

The surface of 1000 SiC (5-7) μm grain size was armored with nickel. (SiC+Ni) particulate was scattered on a stainless steel plate of 0.5 mm thickness and by dropping a body of 0.6 kg from 10 cm the particulates were embedded into a surface of 3.5 mm diameter, repeating the process 60 times. In case of N5 sample of the same steel the body of 0.6 kg was dropped from 20 cm and the particulates were embedded into a surface of 3.5 mm diameter repeating the process 60 times. The total hardened surface was 6 cm^2. After embedding the sample was cleaned by ultrasonic shaking in distilled water, then dried and the imperfectly embedded particulates were removed by Scotch-tape breaking test. The original hardness of the steel was 34 HV.

Sample denomination	N4	N5
Mass after hardening (g)	5.53485	5.33825
Mass before hardening (g)	5.53475	5.33785
Extra mass (g)	0.00010	0.00040

$4x10^{-4}$ g= 6.6 g/cm^3 x 0.00001 cm x 6 cm^2 measured in case of sample N5 corresponds to a SiC coating of 0.1 μm of average thickness, which corresponds with a SiC concentration of nearly 2% in case of particulates of 5 μm grain size.

Taking the hardness of SiC (Ni) also 2500 HV, the expected hardness after surface treating is:

$$34 \times (1-0.02) + 0.02 \times 2500=83.3.$$

So the calculated hardness was 83.3 corresponding well with the actual value of hardness measured: 86 HV, if we take the density of composite 6.6 g/cm^3 obvious from the density of SiC (3.27 c/cm^3) and the density (8.9 g/cm^3) of Ni film armored particulates.

Example 5

One of the driving surface of the two parallel rails of 300 m length running on a curved passage was greased altogether ten times every three days with a gel-like, grease-like mixture of 10% of 1000 SiC particulate and 10% of Fe(2)O(3) of 1-2 μm grain size dispersed in solid organic carrier.

Trains containing 6600 pairs of shafts ran daily on each rail embedding hard particulates onto the driving surface of the greased passage of the rail by an axle load of 0.5-2.5 GPa. Both at the beginning and at the end of the month the hardness of the pair of rails was measured at 16 measuring spots and average wear was calculated as shown in the Table below.

	length (m)	No.of shafts	No.of greases	wear (mm)	Hardness (HB)
Treated rail	300	6600	10	0.111	320
Reference rail	300	6600	-	0.259	262

Due to lubrication the surface hardness of the treated rail increased by 22%, whereas the wear compared to that of the reference rail decreased to its 0.43 times. So the useful life expectancy of the rail increased by 2.3 times due to surface hardening and lubrication. As on the surface of the rail-wheel the particulates were embedded as well due to the high pressure, a similar increase of their useful life can be forecast.

Applications described in the invention show only examples of possibilities of application of the invention. It does not mean however the limitation of the invention to the examples shown hereby. The invention keeps the right of applications not shown here, which can be realized by combining the methods described in the invention.

The advantages of the method according to the invention:
The hard surface on the surface of metals and alloys is produced by the high pressure available during their production or use. During the method a wear-resistant coating of carbide, oxide, nitride, boride or the mixture thereof e.g. carbo nitride or oxinitride can be formed on the surface of metals and alloys.

According to the method described in the invention it is especially advantageous to apply such particulates of hard material for hardening of metal surfaces, the surface of which was previously armored with a layer of metal and/or alloy and/or enfolded with carbon, which build alloy with the base metal to be treated at a low temperature.

The method according to the invention can be mainly applied to protect metal surfaces from wear and corrosion. Most part of hard particulates embedded into the surface resist chemical effects as well so it can be used successfully against chemical-mechanical kind of wear and corrosion.

Table I. : List of hard materials as examples applicable in the composition according to the invention.

Hard materials	**Knoop hardness (Vickers:HV)**
Iron Oxide (FeO)	430
Iron Oxide (Fe(3)O(4))	560
Iron Oxide (Fe(2)O(3))	(700)
Quartz (Silicon Dioxide))(SiO(2))	820
Cementite (Iron Carbide) (Fe(3)C)	1025
Zirconia (ZrO(2))	1160
Iron nitride (FeN)	(1200)
Zirconium Boride (ZrB(2))	1550
Chromium Carbide (Cr(3)C(2))	1735
Chromium Boride (CrB(2))	(1800)
Sialon	(1800)
Chromium Nitride (CrN)	(2500)
Titanium Aluminum Nitride (TiAlN)	(2600)
Molybdenum Carbide (MoC)	1800
Zirconium Nitride	(2800)
Titanium Nitride (TiN)	1800 (2900)
Tungsten Carbide (WC)	1880
Tantalum Carbide (TaC)	2000
Alumina (Al(2)O(3))	2100
Zirconium Carbide (ZrC)	2100
Titanium Carbide (TiC)	2470
Silicon Carbide (SiC)	2480 (2500)
Aluminum Boride (AlB(2))	2500
Chromium Oxide (CrO(2))	(3000)
Iron Boride (FeB)	(3000)
Tungsten nitride (WN)	(3250)
Diamond Like Carbon (DLC)	(3500-4000)
Titanium Carbonitride (TiCN)	(4000)
Vanadium Carbide (VC)	2660
Boron Carbide B(4)C	2750
Silicon Nitride (Si(3)N(4))	3500
Titanium Diboride (TiB(2))	4400 (3000)
Cubic Boron Nitride (cBN)	4600
Boron Carbonitride (cBC(2)N)	(7500)
Diamond	7000 (10000)

CLAIMS

1.Method of making wear resistant surface coating, characterized by that,

- incorporation of particulates to the surface of metals
-hard metal oxides, preferably Al(2)O(3), Fe(2)O(3), Fe(3)O(4) or SiO(2),
-carbides, preferably SiC, Fe(3)C vagy B(4)C,
-nitrides, preferably cBN, CN(x) or TiN,
-borides, preferably FeB or TiB(2)

and/or particulates of compound mixtures of said materials, preferably boron-carbo-nitride or titanium-carbo-nitride or silicon-oxi-nitride and/or particulates of mixtures of said materials is provided by the incorporation of

-particulates comprising of different hard materials,
-or mixtures of particulates of said hard materials,
-or liquid suspensions of these particulates or mixtures of said particulates ,
-or components of a carrier of gel-like emulsion of these particulates or components of mixtures of said particulates,
-or dispersed components of a solid carrier comprising of said particulates and mixtures of said particulates

is attained by application to the frictioning interface of metals and alloys by pressure of preferably 400-5000 MPa that is available during either the production or the use of these metals or alloys and in some instances, the procedure is repeated with decreasing grain sizes consecutively, until the required surface roughness is achieved.

2. Method according to claim 1 characterized by that, the surface of said hard oxides, carbides, nitrides or borides and mixtures of said materials is coated with a layer of metal or alloy, which builds alloy with the material of the surface to be coated.

3. Method according to claim 1 or 2 characterized by that, on the surface of the grains of said particulates enfolded with a hard carbon-base layer of DLC and/or amorphous carbon is made by a mechanical, thermal or other method: such as e.g. pyrolysis, CVD or plasma deposition.

4. Method according to any of claims 1 to 3 characterized by that, hard grains of different particle size and materials are used in said particulates in the same time and surface hardness, roughness and friction coefficient of the metals and alloys is set by changing the weight ratio or grain size of natural and/or armored and/or enfolded particulates.

5. Method according to claim 4 characterized by that, in said particulates the carbon-base enfolded particulates are in 3-80 weight percent, the metal or alloy-base armored

particulates are in 20-97 weight percent applied together and the value of surface hardness, roughness and friction coefficient is set by the weight ratio of carbon-base enfolded and/or metal or alloy-base armored particulates and/or the weight ratio of materials of different grain size.

6. Method according to any of claims 1 to 5 characterized by that, during the method certain different grain size surface-hardening fractions are applied consecutively, in given case during several cycles applying decreasing grain sizes and the surface roughness is set this way.

7. Method according to any of claims 1 to 5 characterized by that, during the method several surface hardening materials of different grain size are applied, and they are embedded in the surface in a single cycle.

8. Method according to any of claims 1 to 7 characterized by that, said liquid comprises of water and at least one dispersion agent and it is applied to the surface by spraying or vaporization.

9. Method according to any of claims 1 to 7 characterized by that, said liquid comprises of oil or at least one type of dispersion agent and it is applied to the surface by spraying or vaporization.

10. Method according to any of claims 1 to 7 characterized by that, said liquid comprises of oil, water and at least one type of emulsion agent and dispersion agent and it is applied to the surface by spraying or vaporization.

11. Method according to any of claims 1 to 7 characterized by that, the mixture of hard natural particulates, enfolded and armored particulates is applied to the surface to be treated by lubrication as gel-like emulsion.

12. Method according to any of claims 1 to 7 characterized by that, said solid carrier comprises of ice and is applied to the surface by greasing and/or melting.

13. Method according to any of claims 1 to 12 characterized by that, the carrier contains inorganic lubricants, such as e.g. graphite, MoS(2), Cu respectively mixtures of said materials.

14. Method according to any of claims 1 to 12 characterized by that, organic lubricants, such as e.g. PTFE (polytetrafluorethylene), polyethylene, polyamide, paraffin, stearin, respectively mixtures of said materials are used as carriers.

15. Method according to any of claims 1 to 12 characterized by that, solid organic lubricants, such as e.g. polyethylene, polyamide, paraffin, stearin, and solid inorganic lubricants, such as e.g. graphite, MoS(2), Cu are used together as carriers.

16. Method according to any of claims 1 to 15 characterized by that, *that* the carrier comprises of 1-30 weight percent dispersed particulates, 1-10 weight percent friction reducer organic and inorganic lubricants and 40-98 weight percent organic lubricant.

17. Composition of materials suitable for making wear resistant surface coating for application preferably during method according to claims 1 to 16, characterized by that, the composition of materials comprises oxides and/or borides and/or nitrides and/or carbides as surface hardening materials.

18. Composition of materials according to claim 17 characterized by that, the surface hardening material is:

- natural particulates (grains of their own) or mixture of particulates, and/or
- particulates, which are armored with metal or alloy coating and/or
- particulates, which are enfolded with carbon based coatings (DLC –diamond-like hard carbon coating and mixture of amorphous carbon and graphite) or mixture of said materials.

19. Composition of materials according to any of claims 17-18, characterized by that, the surface hardening materials, particulates are preferably

- hard particulate oxides, which are the mixtures of metals in columns 4b, 5b, 6b of the periodic table, as well as compounds of Al, Si and Fe with elements B, C, O, N and mixtures of said particulates, moreover mixture compounds of said elements and materials containing in given case solid lubricant, reducing friction.

20. Composition of materials according to claim 19, characterized by that, the surface hardening material comprises preferably oxides, such as aluminum oxide (Al(2)O(3)), iron oxide (III) (Fe(2)O(3)), iron oxide (Fe(3)O(4)), titanium dioxide (TiO(2)),or silicon-dioxide (SiO(2)), magnesium oxide (MgO), or other hard oxides,
carbides, such as silicon carbide (SiC), iron carbide (Fe(3)C), tungsten carbide (WC), or boron carbide (B(4)C), or other hard carbides,
nitrides, such as boron nitride (cBN), or carbo nitride (CN(x)) or titanium nitride (TiN), silicon nitride (Si(3)N(4)), aluminum nitride (AlN), titanium nitride (TiN), tantalum nitride (TaN), iron nitride (FeN), molybdenum nitride (MoN), tungsten nitride (WN), or other hard nitrides,
borides, such as iron boride (FeB), titanium-diboride (TiB(2), aluminium-diboride (AlB(2)), chromium boride (CrB(2)), zirconium-boride (ZrB(2), or other hard borides,
or mixtures of these materials, such as boron carbo nitride (cBC(2)N), titanium carbonitride (TiCN) or silicon oxi-nitride (SiON), aluminium titanium oxide (Al(x)Ti(y)O(z)), or other hard mixtures of compounds, respectively and mixtures of these materials.

21. Composition of materials according to any of claims 17 to 20, characterized by that, the grain size of the particulates in the material applied for surface hardening is in 1 mm-2nm range.

22. Composition of materials according to any of claims 17 to 21, characterized by that, the hard particulate is dispersed in liquid suspension, said liquid suspension carrier comprises of

- preferably water and surfactant and dispersing agent,
- mineral-, and/or vegetable-, and or synthetic-oil and emulsion agent, or
- water, and/or mineral, and/or vegetable-, and/or animal- and/or synthetic-oil and emulsion agent,

furthermore in given case anticorrosion agent.

23. Composition of materials according to claim 22, characterized by that, in a preferred embodiment the composition of materials comprises of 1-30 weight percent hard particulates dispersed in liquid, 55-98 weight percent liquid carrier, 1-10 weight percent solid friction reducing lubricant and 0.1-5 weight percent corrosion inhibitor.

24. Composition of materials according to any of claims 17 to 21, characterized by that, the surface hardening material consisting of hard particulates is dispersed in a gel-like material, which carrier in given case consists of
-vegetable and/or animal-, and/or mineral, and/or synthetic oil, or
-palmitic and stearic acid mixture, or
-mixture of oil and solid paraffin, or
-mixture of solid paraffin, stearic acid and oil, furthermore in given case corrosion inhibitor.

25. Composition of materials according to claim 24, characterized by that, in a preferred embodiment the gel-like material consists of 1-30 weight percent hard particulate dispersed in grease, 55-98 weight percent grease carrier, 1-10 weight percent solid friction reducing lubricant as well as 0.1-5 weight percent corrosion inhibitor.

26. Composition of materials according to claims 17 to 21, characterized by that, the surface hardening material comprising of hard particulates is dispersed in a solid carrier, and said solid carrier consists of:

- ice, or
- paraffin, stearic acid and mixture thereof and surfactant, or
- plastics, such as polyamide (Nylon), polyethylene (PE), polytetrafluorethylene (PTFE) or other plastics with low friction coefficient,

furthermore in given case friction reducer and/or corrosion inhibitor.

27. Composition of materials according to claim 26, characterized by that, in a preferred embodiment the composition consists of hard particulate dispersed in solid carrier by 1-30 weight percent, solid carrier by 55-98 weight percent, solid friction reducing lubricant by 1-10 weight percent, furthermore corrosion inhibitor by 0.1-5 weight percent.

28. Composition of materials according to claims 17 to 27, characterized by that, the composition consists of hard particulates that have previously been enfolded in hard carbon coating (DLC, mixture of graphite and amorphous carbon) to reduce friction, furthermore solid lubricants (graphite, PTFE, iron oxides, MoS(2), TiO(2), hexagonal boron nitride) are added to further decrease friction coefficient.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/HU2005/000061

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C24/02 B24D18/00

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 7 C23C B24D

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)

EPO-Internal, PAJ, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 10, 31 August 1998 (1998-08-31) & JP 10 121166 A (KAYABA IND CO LTD), 12 May 1998 (1998-05-12)	1,4-9, 17-22
Y	abstract	2,3, 10-16
X	WO 00/08232 A (LAYSTALL ENGINEERING COMPANY LIMITED; BOWERS, MARTIN, ROBERT) 17 February 2000 (2000-02-17)	1,4-7, 17-22
Y	page 1, line 21 - page 3, line 6; claims 1-14	2,3, 10-16
X	WO 98/45092 A (SUNG, CHIEN-MIN) 15 October 1998 (1998-10-15)	1,4-7, 17-21
Y	page 26, line 26 - page 28, line 3; claim 2; figures 5A-5D	2,3, 10-16

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 September 2005	13/10/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hoyer, W

INTERNATIONAL SEARCH REPORT

International Application No
PCT/HU2005/000061

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 856 709 A (DELLA PORTA P ET AL) 24 December 1974 (1974-12-24)	1,4-7, 17-21
Y	column 3, lines 39-49; example 1	2,3, 10-16
X	US 4 485 757 A (EBNER ET AL) 4 December 1984 (1984-12-04)	1,4-7, 17-21
Y	column 2, lines 52-62	2,3, 10-16
	column 4, lines 63-65	
X	WO 94/25641 A (WEDLAKE, ROGER, JOHN; STRYDOM, IZAK, LE ROUX; PRINS, JOHAN, FRANS; ROM) 10 November 1994 (1994-11-10)	1,4-7, 17-21
Y	claims 1-13	2,3, 10-16
X	FR 1 021 094 A (BAUDSON, ROGER-MARCEL) 13 February 1953 (1953-02-13)	1,4-7, 17-21
Y	claims 1-3; figure 1	2,3, 10-16
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 290 (C-447), 18 September 1987 (1987-09-18) & JP 62 083480 A (KUBOTA LTD; others: 01), 16 April 1987 (1987-04-16)	1,4-7, 17-21
Y	column 4, paragraph 2 abstract	2,3, 10-16
X	EP 0 642 889 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 15 March 1995 (1995-03-15)	17-28
Y	page 6, line 5 - page 8, line 31	2,3, 10-16
	page 13, lines 14,15	
Y	PATENT ABSTRACTS OF JAPAN vol. 018, no. 572 (M-1696), 2 November 1994 (1994-11-02) & JP 06 210326 A (NIPPON STEEL CORP; others: 02), 2 August 1994 (1994-08-02) abstract	10-16

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1 (partially), 17 (partially), 18 (partially), 19 (partially), 20 (partially)

Present claims 1 and 17 - 20 refer to "particulates" comprising an extremely large number of possible compounds. Support and disclosure in the sense of Article 6 and 5 PCT is to be found, however, for only a very small proportion of the compounds claimed, see examples 1 - 5 in the description. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1 and 17 - 20 (PCT Guidelines 9.19 and 9.23).

The search of claims 1 and 17 - 20 was restricted to those claimed compounds which appear to be supported, namely those disclosed in Examples 1 - 5, in particular, SiC and Al2O3.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/HU2005/000061

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/HU2005/000061

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