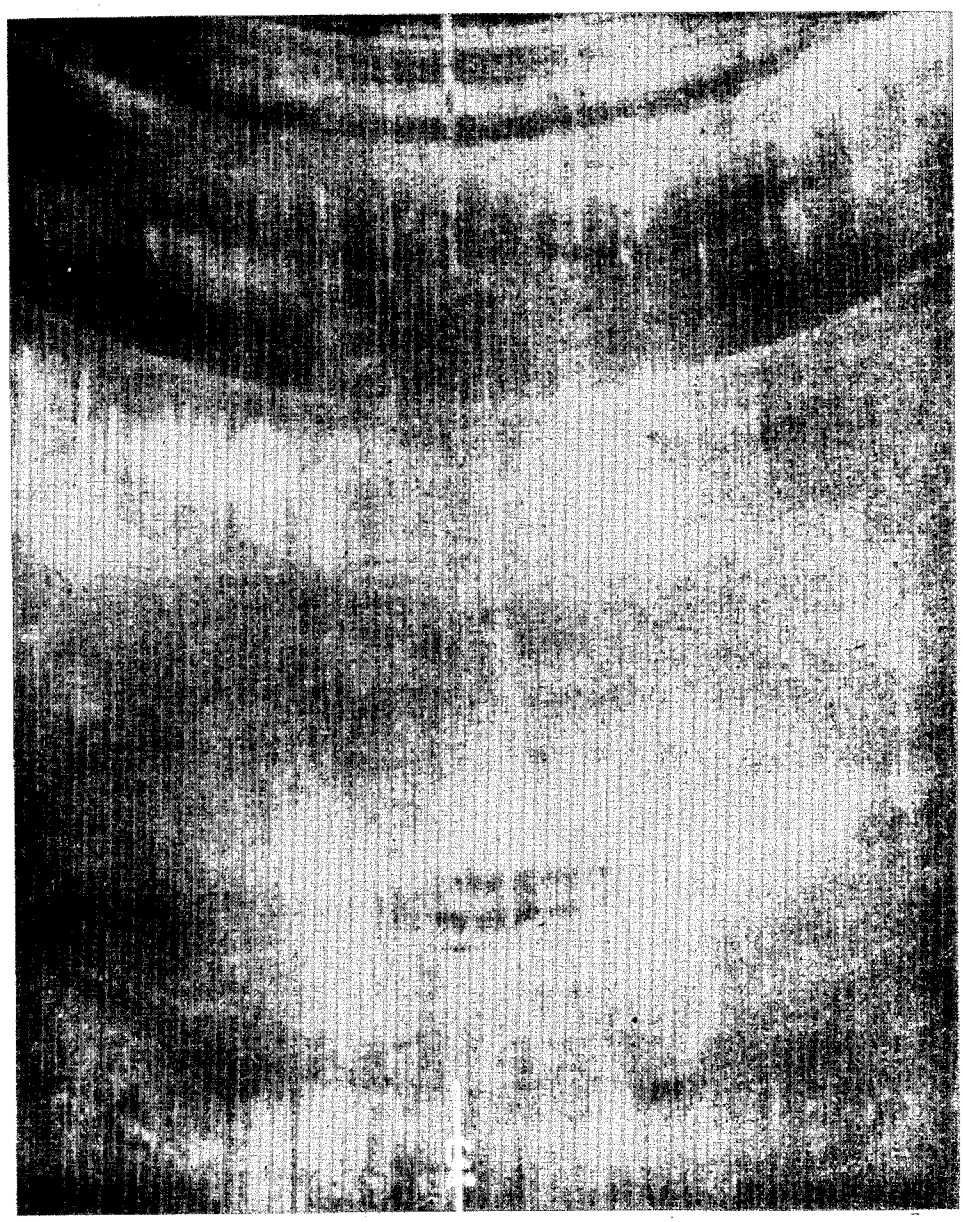
Dec. 19, 1950 H. M. BRAMBERRY 2,534,406

COATED METAL ARTICLE AND METHOD OF MAKING THE SAME

Filed Sept. 22, 1944 5 Sheets-Sheet 1

Fig. 1



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COATED METAL ARTICLE AND METHOD OF MAKING THE SAME

Filed Sept. 22, 1944 5 Sheets-Sheet 2

Fig. 2



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COATED METAL ARTICLE AND METHOD OF MAKING THE SAME

Filed Sept. 22, 1944 5 Sheets-Sheet 3

Fig. 3



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COATED METAL ARTICLE AND METHOD OF MAKING THE SAME

Filed Sept. 22, 1944 5 Sheets-Sheet 4

Fig. 4



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COATED METAL ARTICLE AND METHOD OF MAKING THE SAME

Filed Sept. 22, 1944 5 Sheets-Sheet 5

Fig. 5

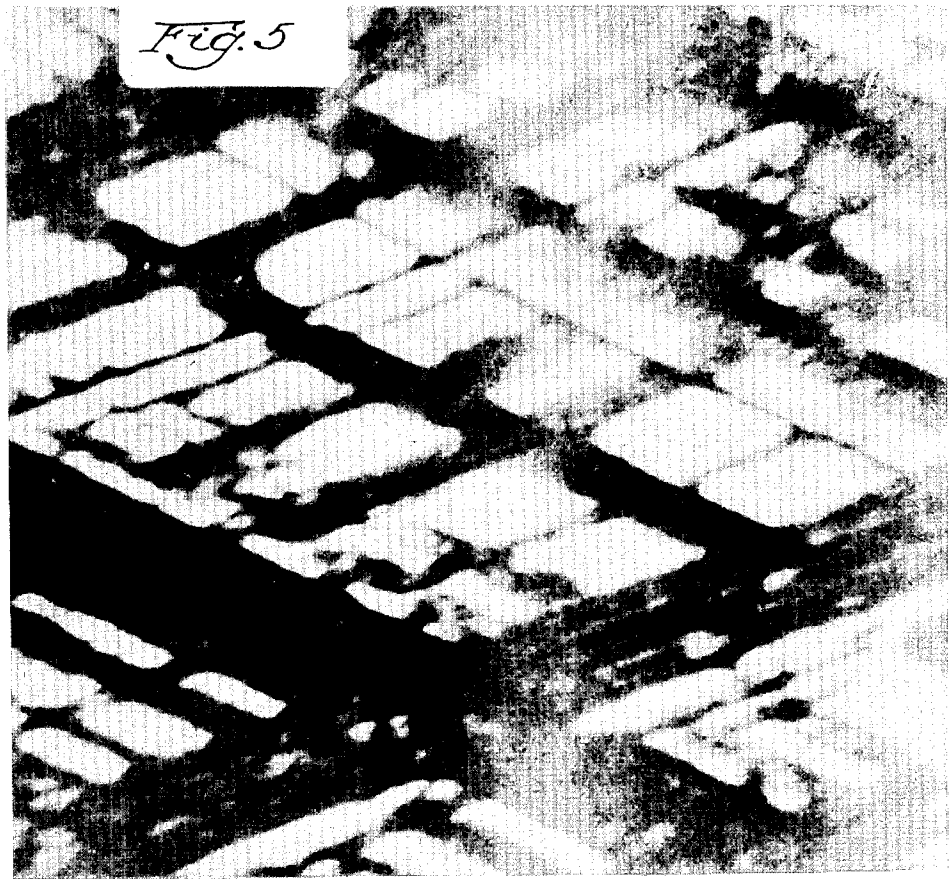


Fig. 6

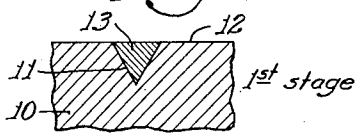


Fig. 7

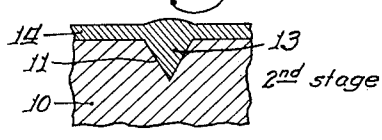


Fig. 8

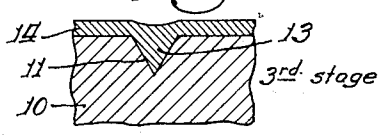


Fig. 9

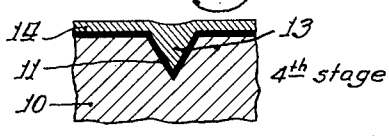
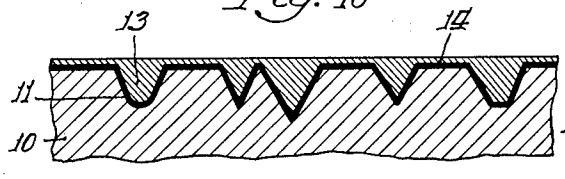


Fig. 10



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Patented Dec. 19, 1950 2,534,406

UNITED STATES PATENT OFFICE

2,534,406

COATED METAL ARTICLE AND METHOD OF MAKING THE SAME

Harry M. Bramberry, New Castle, Ind.; Harry M. Bramberry, Jr., administrator of said Harry M. Bramberry, deceased, assignor, by direct and mesne assignments, to himself

Application September 22, 1944, Serial No. 555,377

16 Claims. (Cl. 309—2)

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This invention relates to metal wear surfaces and methods of "filling" such surfaces including particularly internal combustion and other compression engine cylinders, pistons and piston rings, for improving the operating characteristics thereof, including effecting the proper running-in of the parts, which results in minimum oil consumption, and low blow-by, for long periods of operation.

One of the major difficulties in the manufacture of internal combustion and other compression engines, is the provision of proper cylinder surface conditions which will impart to the piston and ring wear surfaces the desirable surface characteristics to establish the necessary initial compatibility of these surfaces under load and temperature conditions.

It is a prime object of this invention to provide an improved metal wear surface and method for filling such surfaces with compounds that are particularly applicable to the filling of relieved internal combustion and other compression engine cylinders, to provide a surface condition that promotes compatibility of the parts in the shortest possible initial run-in time.

It is a more particular object to provide a novel method of applying the compound which may be readily accomplished at ordinary room temperatures, and which forms a tenacious and firm bond with the metal, as well as providing polishing means, imparting to the piston and ring surfaces an optimum surface finish, which it has been found, materially improves and shortens the green or run-in time of cylinders so treated and also greatly enhances the operating life of such cylinders.

It is a further object of this invention to provide a novel method of bonding a filler compound to the metal surface which results in control of the thickness dimension making it practicable to provide an appreciable radial thickness of filler effective to let the cooperating surfaces of pistons, piston rings and cylinder come into engagement gradually in a manner producing optimum compatibility.

It is a further object to provide a novel method of applying a filler compound to the metal surfaces which results in a bond between the filler and the metal that increases in hardness as the underlying metal surface is approached whereby to compensate for any machined or other irregularities in the metal parts, including in particular any irregularities in the peripheral wall of a cylinder.

It is another object to provide a cylinder internal surface character and pattern in relief that is particularly adapted to have the intervening recessed channels of a depth which may result in an oil consumption which may be slightly higher than normal, which arrangement is particularly effective for the application and reception of a filler compound bonded thereto and functioning to further control the wear-in between the cylinders and rings as well as functioning to control the oil consumption.

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A still further object is to provide a novel wear surface for relieved cylinder surfaces, as well as a novel method of applying said compound to said surface which results in the formation of a graphitic film, firmly bonded to the surface base metal and which has the highly desirable properties of abrasion resistance to effect a polishing action to materially decrease the green or run-in time and prevent scuffing, such film also possessing a wetting effect to secure optimum boundary lubrication and lubricant retaining properties, thus enabling the establishment of a lacquer-like film over the entire compression ring surface area after the run-in period is completed.

Other more particular objects, advantages and uses of my invention will become apparent from a reading of the following specification taken in connection with the accompanying drawings which form a part thereof and wherein:

Fig. 1 is an actual photograph of approximately one-half of the interior surface of a standard production cylinder, not employing my invention, said surface showing the major thrust side thereof and indicating the condition of the surface after the green and final runs;

Fig. 2 is an actual photograph of a similar portion of the interior surface of the same standard production cylinder of the minor thrust side thereof after the green and final runs;

Fig. 3 is an actual photograph of approximately one-half of the internal surface on the major thrust side of a cylinder identical to the above cylinder but formed with my scratched-cross-hatched pattern in relief, with a superimposed plateau surface, and the interior surface being filled with the compound in the manner of the preferred embodiment of my invention;

Fig. 4 shows an actual photograph of a portion of the same cylinder as Fig. 3 but on the minor thrust side thereof;

Fig. 5 shows an actual photograph of a greatly enlarged (substantially 100 to 1) representative portion of a cylinder interior that has been

filled in accordance with the preferred embodiment of my invention and actually operated under severe conditions in a high out-put internal combustion engine; and

Figs. 6 to 9, inclusive, are enlarged sectional views showing the character of the surface of the cylinder of Fig. 5 during different stages of the filling thereof, in accordance with my invention, and

Fig. 10 is an enlarged sectional view of the cylinder wall of the surface relieved type, after the filling process has been completed and the cylinder has been operating in the engine during the green or run-in period.

Referring now to the drawings, it is believed that a clear understanding of the nature of the present invention may be best had by a comparison of actual photographs of cylinder surfaces treated in accordance with the principles of the present invention, with photographs of cylinders finished in accordance with conventional present-day methods. Figs. 1 and 2, are actual photographs of the major and minor thrust sides of a standard production steel cylinder following the green and final runs. Figs. 3 and 4, on the other hand, are actual photographs of the major and minor thrust sides of similar cylinders, following the green and final runs, said cylinders having been processed in accordance with the present invention. An inspection and comparison of these photographs will clearly show the remarkably improved results secured by my invention.

The cylinder of Fig. 1 was finished in accordance with conventional practice which seeks to produce a mirror-like surface finish. The roughness of such a surface in accordance with present-day practices is of the order of 10 R. M. S. Figs. 1 and 2 clearly show that the cylinder is now fatally defective, and in operation results in excessive oil consumption. This is due to the surface disturbance or cold-worked condition shown on these figures, such condition being evidenced by the vertically extending white streaks, as well as by the horizontally extending disturbed bands at various levels. These streaks and bands represent surface disturbance areas generally referred to as scuffing or scoring, which are imparted by the action of the piston and rings, and would result in excessive blow-by and high oil consumption.

Turning now to Figs. 3 and 4, the comparison thereof with Figs. 1 and 2 is outstanding. The cylinder surface of Figs. 3 and 4 shows ideal compatibility between piston and piston rings on the one hand, and the cylinder on the other. The scratched, cross-hatched relief pattern with intervening piston and ring supporting plateau surfaces shows no evidence of surface disturbance. There is no significant evidence of piston ring or piston skirt cross-head action or marking, such as is present in Figs. 1 and 2.

It is also pointed out that the pistons as well as the rings removed from the cylinder of Figs. 3 and 4 showed even more remarkable results, further substantiating the importance of my invention. This was evidenced by the fact that while identical pistons and rings were used in the comparative test, the rings from the cylinder of Figs. 1 and 2 were worn and smooth, while those from the cylinder of Figs. 3 and 4 still contained the original tool marks thereon.

Turning now to Fig. 5 it is believed that the important aspects of my invention can be further understood by reference to the actual enlarged photograph of a portion of the ring engaging surface of an internal combustion engine cylinder treated in accordance with a preferred embodiment of my invention. This photograph brings out clearly the results of actually filling a relieved cylinder surface with my improved filler compound in the novel manner herein disclosed. This particular cylinder is of the scratched, cross-hatched superimposed plateau type similar to that of Figs. 3 and 4. The white diamond-like shaped areas indicate the plateau surfaces against which the rings actually operate while the intervening darker areas are composed of my filler compound bonded to the relieved channels or recesses. While the plateau areas show up in white in the photograph, it is important to note that the entire ring travel area of the cylinder when removed from the engine following operation under the most severe conditions, was actually uniformly coated with a very thin brownish lacquer-like film. This uniform lacquer coating results only when optimum antifriction conditions, optimum oil control conditions and optimum heat removal conditions prevail. All of these optimum conditions are evidenced in the structure disclosed in this photograph of Fig. 5 as well as the photographs of Figs. 3 and 4. These photographs show unusual results never heretofore even approached, so far as I am aware.

Turning to Fig. 10, I have indicated schematically a cross-sectional view taken through the wall of the cylinder shown in Fig. 5 for the purpose of more readily identifying the component parts of the structure involved and describing the manner in which the filling is accomplished. The cylinder here employed for the purpose of describing a preferred embodiment of my invention comprises a section of a cylinder 10 having first formed therein a character or pattern preferably by means of scratched, cross-hatched honing to provide recessed scratches 11 to the depth of at least .0002" and deeper. This cylinder had a relieved area of the order of 35 per cent and a corresponding unrelieved area made up of a multiplicity of substantially uniformly disposed pyramidal protuberances having plateau surface areas 12 which form individual areas. This ratio may vary however from 15 to 60 per cent in relief. I have found however, that for a steel cylinder used in a high compression military aircraft engine, the 35 per cent of relief is most effective. This particular construction of cylinder wall surface, apart from its novel combination with the present improved filler compound and method of applying the same with the accompanying important product and unusual results obtained, forms the subject matter of my application Serial No. 555,379, filed September 22, 1944, for Cylinder Surface Character, now Patent 2,434,880 of January 20, 1948.

Relieved grooves or recesses 11 of a cylinder, thoroughly cleaned of any oil film are first filled to the level of the plateau areas 12 with a compound that will be referred to as a trowelling compound indicated generally at 13, which is of a relatively putty-like consistency. Following this the surface is sprayed with a compound in liquid suspension which will be referred to as the spraying compound indicated generally at 14. The cylinder is next preferably allowed to dry for several hours and then baked at an elevated temperature, preferably between 400 and 600° F., the baking conditions being determined by the desired degree of hardness of the bond between

the underlying metal and the filler, as well as by the desired abrasion resistant character to be imparted to the filler. The longer the baking time, in general the harder the bond will be and the more abrasion resistant character of the resultant surface.

My improved trowelling compound consists of a fine or colloidal graphite base, homogeneously mixed with a plasticizer, in the ratio of one to two parts by weight, respectively. I have found that tricresyl phosphate when employed as the plasticizer yields excellent results, although good results may be obtained by utilizing any of the well-known materials commonly used in plasticizing paints, such as diamyl phthalate or castor oil. While I prefer to employ the materials in the above ratio, this may be varied if desired, it being pointed out, however, that if too large a percentage of plasticizer is used, the compound remaining in the channels will be subject to an undesirable degree of shrinkage, during the subsequent operations. The graphite used should be ground to colloidal size, the resultant particles being of the order of 5 to 10 microns. I have found that this small size is most effective in filling the minute channels of the relieved cylinders.

My improved spraying compound comprises preferably a water in oil emulsion and consists of a fine or colloidal graphite base, a binder, phosphoric acid, a carrier thinner or solvent, and a suitable emulsifier.

There is given below by way of example, one formula for making one gallon of a spraying compound which is a water in oil emulsion and which I employed in treating the cylinders shown in Figs. 3, 4 and 5.

Material	Gallons	Pounds	Percentage by Weight
Binder	.082	.685	7.78
Phosphoric Acid (75% by volume)	.081	1.088	12.35
Graphite (finely ground)	.099	1.565	17.75
Solvents for the resin binder	.716	5.303	60.15
Emulsifier	.022	.175	1.97
	1.000	8.816	100.00

The solvents employed in the above formula comprised the following, in the ratios noted.

Material	Gallons	Pounds
Xylol	.392	2.760
High Flash Solvent Naphtha	.080	.510
Water	.244	2.033
	.716	5.303

In the above formula, the binder is preferably a resin and may be of the class of petroleum or vegetable residue pitches, it being understood, however, that other suitable resins may be employed if desired. The binder used is preferably water insoluble, should be such as to have a good cohesive or cementing action with the graphite, and should be one which does not completely volatilize at the high temperatures of the order of 400° to 600° F. which may be employed in the process to hasten the action of the spraying compound. The physical characteristics of the binder are preferably as follows:

1. Softening point from 155° to 170° F.
2. Penetration from 25 to 35.
3. Stormer viscosity at 360° F. of from 30 to 60 R. P. M.

With respect to the acid employed, this is preferably ortho-phosphoric. Other phosphoric acids such as metaphosphoric acid and phosphoric anhydride have been used, but are ordinarily less satisfactory. In the formula, the acid has been noted as being of a strength of 75% phosphoric acid. In the event the strength is of a greater order, it will be understood that the water content is correspondingly changed, but that the same ratios are maintained.

The graphite utilized may be natural or synthetic, of high quality and preferably of extremely small particle size. It is preferred to use colloidal graphite or at least particles approaching the fineness of colloidal size.

The solvents, employed, are given by way of example only, since they may be any suitable solvent for the resin used.

The emulsifying agent employed must be suitable to emulsify water in oil or oil in water. The agent may be of either the cationic or non-ionic classes. In the specific formula given, the emulsifier used was a substituted polyglycoletheralcohol, an emulsifier of the non-ionic type. However, if desired, the emulsifier may be of the cationic type, such as an amine-amide, for example.

In preparing the spraying compound according to the above formula, the entire amount of resin binder was dissolved in an equal weight of xylol, this resulting in a 50% solids solution. To this solution was added a graphite dispersion which comprised the entire amount of graphite with an equal weight of xylol. This dispersion was thus also a 50% solids product and the combination of the resin solution and graphite dispersion is what is termed the oil phase of the emulsion.

Thereafter, the water phase of the emulsion is obtained by adding the emulsifier and water to the phosphoric acid. Then the oil and water phases are mixed with violent agitation and the resultant emulsion thinned to spraying viscosity with the high flash solvent and the remainder of the xylol. If desired the resultant compound may be filtered or otherwise treated to remove any undesirable agglomerates and to secure a product with the necessary degree of fineness.

While the foregoing, outlines one method of making my improved spraying compound, with certain specific amounts and percentages of materials, I have found that certain of the proportions may be varied within limits, and will yield excellent results.

For example, I have found that I may vary the ratio by weight of graphite to binder to from 2 to 1, to 3 to 1. Best results may be obtained when using an amount of graphite from twice to three times the weight of the binder. This variation has been determined from a wide variety of experiments, and therefrom, I have found that for a ratio higher than 3 to 1, there is a tendency for the resultant film produced by the spraying compound to become thixotropic or jelly-like in nature with accompanying undesirable flow properties. Moreover, the resultant film does not have the desirable degree of abrasion resistance or polishing quality.

I have also found that with ratios of less than 2 to 1, the resultant film is too soft and less resistant to abrasion than that desired. Hence, my preferred range of ratios, which I have determined results in a tenacious film which has the desired degree of abrasion resistance, is that set forth above.

The chemical or phosphoric acid content of the compound is also a very important variable and may be expressed in a ratio such as

$$\frac{\text{Grams of 100\% phosphoric acid}}{\text{Grams of total solids}}$$

In the above ratio, the solids comprise the total weight in grams of the resin binder and the graphite, and I have found that the optimum values of this ratio are from .10 to .80. I have found that when this ratio is below the lower limit, the resultant films are lacking in strength and resistance to abrasion and exhibit a lack of tenacious adherence to the cylinder surface. The degree of polishing effect of such films is decidedly less than that desired in practice. When the ratio exceeds the high limit, the resultant films will not dry properly, and it was found that they would blister regardless of whether the sprayed cylinder was permitted to air dry or was baked. Within the limits prescribed, the resultant films were highly satisfactory and were sufficiently resistant to abrasion, as to give the required high degree of polishing effect.

The spray-on compound is applied at ordinary room temperature to a thickness of the order of from .003" to .001" above the plateau areas. It is preferred that the cylinder so filled be allowed to dry for about five hours in the case of cylinders of steel or iron. In the case of chromium surfaced cylinders, the drying time is preferably about ten hours. Such drying is followed by a baking operation at an elevated temperature, preferably from 40° to 600° F., for a time period of from thirty to sixty minutes to produce the desired abrasion resistance of the filler, as well as to produce the requisite hard phosphate bond between the filler and the underlying metal. In the case of steel and iron cylinders, such bond would be iron phosphate, while in the case of chromium surfaced cylinders, the bond would be chromium phosphate. By increasing the acidity content within the limits heretofore noted, the abrasion resistance can also be increased. It is noted that upon the approach of the maximum permissible acidity content bubbling will be experienced prior to the baking or during the baking operation.

With the proper choice of proportions to fit the circumstances of the particular installation, it is found that a hard phosphate bond results having a final thickness dimension of the order of from .0003" to .001", this bond approaching the hardness of the underlying metal surface proper of a thickness of approximately .00005" to .0001". During the process, the phosphoric acid reacts with the metal of the cylinder surface to form the phosphate in situ and phosphate dispersed throughout the graphite, thus effecting a firm cementing action of the graphite not only within the relieved areas but also on the plateau surface areas.

It is of further importance to note that by filling the cylinder in this manner including the formation of the hard phosphate bond, irregularities otherwise present as a result of error in machining or error due to distortion in operation are compensated for by this hard bond between the filler and the underlying metal. This is very important, since it is substantially impossible to machine or otherwise form a cylinder ring travel surface perfectly symmetrical.

The trowelling-in of the filling compound 13 may be most effectively accomplished by rotating the cylinder while the trowel is held in proper

relation thereto. Fig. 6 shows one of the scratches or grooves 11 filled with the trowelling compound. After this trowelling operation is completed and the excess compound removed as shown in Fig. 6, the spraying compound containing the proper proportion of phosphoric acid is preferably sprayed on in one or more coats, this also being accomplished while rotating the cylinder. While rotation of the cylinder or cylinders is preferable, in applying the trowelling and spray compounds, the invention is not limited thereto, since the cylinder may be stationary if desired. By using a phosphoric acid content within the limits heretofore described, I find that this provides the necessary acidity for the total volume of the trowelling compound and the spray compound, and avoids difficulties such as bubbling of the trowelling compound and an unsatisfactory resultant film. Fig. 7 shows one of the grooves following the application of the spray compound. The trowelled-in compound immediately absorbs the liquid constituents from the spray compound so that the two when combined will chemically react as one for both air drying and baking. Prior to baking, the surface appears like that in Fig. 8. It will be noted that baking is employed primarily to speed up the process, since given sufficient time for air drying the installation of the filler could be accomplished without baking, on steel and iron cylinders. The fact that the present filling compounds can be properly installed and bonded to the wear surface of steel and iron at ordinary room temperatures is considered of particular importance, especially for automotive en-bloc cast iron cylinders. Among the other advantages growing out of this unusual property of the present compounds is the fact that the same may be installed in the field where baking facilities are not available. In comparison, it is noted that from seventy to eighty hours of air drying is required to obtain approximately 90 per cent of the abrasion resistance and hardening accomplished by five to fifteen hours preliminary air drying followed by baking. Following baking the surface is as shown in Fig. 9, the bottom of the depression over the groove being of the order of .0003" to .001" above the base metal of the cylinder.

Further attention is directed to the apparent lubricating phenomena present in a cylinder filled in accordance with the process as above described. Under abnormal engine operating conditions such as that to which the cylinder of Fig. 5 was subjected, it has been found quite common in the usual types of cylinders, for the accompanying detonation to overload the cylinder walls with resulting scoring and scuffing, as well as causing abnormal expansion of the piston. It is noted that no damage is evidenced in the cylinder wall of Fig. 5 and that the same is in substantially perfect condition. It would appear that these unusual results are due in part to the porosity and oil absorbing or retaining nature of the herein disclosed filler compounds, acting in the manner akin to a sponge action to maintain lubricant under abnormal conditions.

As concerns the application of the present inention to relieved cylinder surfaces fundamental importance is attached to the fact that the appreciable thickness dimension of the filler above the metal surface of the order of .0003" to .001", together with the hard bond of iron phosphate in the case of iron and steel and chromium phosphate in the case of chromium surfaced cylinders, results in a gradual wear-in of the

parts which is exemplified in the case of the cylinder assembly by the slow letting down of the rings and piston onto the cylinder wall with the resulting unusual compatibility.

In the foregoing, I have described the combined use of the troweling and spraying compounds in connection with the filling of cylinders which have been relieved in accordance with my application Serial Number 555,379, filed September 22, 1944, for Cylinder Surface Character, now Patent 2,434,880 of January 20, 1948. In that application, and as pointed out herein, the scratched cross-hatched relief pattern provides recesses which are of a depth of at least .0002", and in the event that the maximum depth of the grooves does not materially exceed .0008" the use of the trowelling compound may be dispensed with, in which event one or more coats of the spray compound has been found sufficient to secure the film of desired thickness.

It is also desired to point out that cylinder surfaces, relieved in manners other than by the scratched, cross-hatched method may be filled in accordance with my invention. For example, I have filled cylinders in accordance with the method disclosed herein which were provided with chromium surfaces, relieved electrolytically, with excellent results. The invention is therefore not limited in its application to the filling of cylinder surfaces which are relieved in any particular manner. The invention is furthermore not limited to the treatment of any particular type of metal cylinder and may be employed for treating cylinders of iron, steel, steel alloys, aluminum, bronze, chromium or hardened surfaces, for example. In the case of the treatment of chromium or hardened or alloy steel surfaces, the baking step is a necessary requisite in order to attain a hard, abrasion resistant film. However, I have found that unless the depth of relief, on cylinder surfaces is carried to at least .0002", the exceedingly highly satisfactory results flowing from the present invention and fully set forth herein, will not be obtained.

In the event that my improved spray compound is used to coat or fill the exterior wear surfaces of pistons and piston rings, it will be understood that such surfaces may be relieved, as set forth herein, or may be provided with conventional finishes. I have found that conventional finished surfaces of pistons and piston rings when treated with my spray compound, are such, that when these elements are used in engines, the cooperating parts within the engine power zone exhibit a new and improved compatibility.

While I have described my invention in connection with certain specific applications thereof, it will be understood that this is by way of example rather than limitation and that the same is to be accorded the scope as defined by the appended claims.

1. An engine cylinder having a plurality of channels or grooves formed in the ring-engaging surface thereof, and having a continuous film bonded to said surface and within the channels, said film comprising a phosphate of the metal of the surface and fine graphite.

2. An engine cylinder having relieved areas throughout the ring-engaging surface thereof, and having a continuous film on said surface and extending into said areas, said film comprising fine graphite firmly bonded to the surface and areas by a phosphate of the metal of the surface.

3. An engine cylinder having relieved areas throughout the ring-engaging surface thereof, said areas being of a depth of at least .0002", said surface having a continuous film thereon and extending into said relieved areas and including graphite and a binder uniformly bonded to the surface and areas by a phosphate of the metal of the surface.

4. An engine cylinder having a chromium ring-engaging surface provided with a plurality of relieved areas, said surface having a continuous film thereon extending into said areas, and comprising fine or colloidal graphite bonded to the surface and areas by chromium phosphate.

5. An engine cylinder having a ferrous metal ring-engaging surface provided with a plurality of relieved areas, said surface and areas having a thin, continuous film thereon comprising fine graphite firmly bonded to the surface and areas by iron phosphate.

6. An engine cylinder having an internal ring-engaging surface formed into a pattern in relief, said surface having a thin, continuous film thereon, said film comprising fine graphite firmly bonded to the surface by a phosphate of the metal of said surface area.

7. An engine cylinder having an internal ring-engaging surface formed into a pattern in relief, said pattern including a plurality of grooves defining a plurality of protuberances having plateau surfaces forming a ring-engaging area, said area and grooves having a thin, continuous film thereon, said film including fine graphite firmly bonded to the area by a phosphate of the metal of said surface.

8. An engine cylinder having an internal scratched, cross-hatched surface having character or pattern in relief and including a multiplicity of protuberances separated by said scratches and terminating in ring-engaging plateaus, and a thin, continuous film deposited on said plateaus and within said scratches, said film comprising fine graphite bonded in place by a phosphate of the metal of said surface.

9. The method of increasing the load-carrying capacity of the wear surface of an engine cylinder and improving the compatibility between the wear surface and the piston and piston rings, which consists in relieving at least the ring-engaging part of the wear surface substantially uniformly throughout its area by removing from 15 to 60 per cent of the metal surface to a depth of at least .0002 inch, then filling the relieved areas and covering the unrelieved areas with a compound comprising an emulsion of a fine or colloidal graphite, a resin binder, phosphoric acid, a solvent for the resin binder, and an emulsifier, the ratio by weight of graphite to binder in the compound being from 2:1 to 3:1 and the ratio by weight of 100% phosphoric acid to binder and graphite being from 0.10 to 0.80, and then bonding the compound to the metal of the relieved and unrelieved areas.

10. The method of increasing the load-carrying capacity of the wear surface of an engine cylinder and improving the compatibility between the wear surface and the piston and piston rings, which consists in relieving at least the ring-engaging part of the wear surface substantially uniformly throughout its area by removing from 15 to 60 per cent of the metal surface to a depth of at least .0002 inch, then filling the relieved areas and covering the unrelieved areas with a compound comprising an emulsion of a fine or colloidal graphite, a resin binder, phosphoric acid, a solvent for the resin binder, and an emul-

sifier, the ratio by weight of graphite to binder in the compound being from 2:1 to 3:1 and the ratio by weight of 100% phosphoric acid to binder and graphite being from 0.10 to 0.80, and then bonding the compound to the metal of the relieved and unrelieved areas by drying the compound and then baking it.

11. The method of treating the wear surface of an engine cylinder to improve the load-carrying capacity thereof and to control the flow of oil past the piston, comprising the steps of relieving at least the ring-engaging part of the wear surface substantially uniformly throughout its area by removing from 15 to 60 per cent of the metal surface to a depth of .0002 inch or more, filling said relieved areas to a substantially flush condition with a material comprising fine or colloidal graphite and a plasticizer, covering the filled and unfilled areas with a compound which impregnates the material filling the relieved areas and which comprises an emulsion of a fine or colloidal graphite, a resin binder, phosphoric acid, a solvent for the resin binder, and an emulsifier, the ratio by weight of graphite to binder in the compound being from 2:1 to 3:1 and the ratio by weight of 100% phosphoric acid to binder and graphite being from 0.10 to 0.80, and then bonding said material and said compound to the relieved and unrelieved areas of the wear surface by causing the phosphoric acid of said compound to react with the metal of said relieved and unrelieved areas.

12. An engine cylinder having a chromium ring-engaging surface provided with a plurality of relieved areas having a depth of at least .0002 inch, said surface having at least initially a continuous film thereon extending into said areas and comprising fine or colloidal graphite bonded to the surface and areas by chromium phosphate.

13. An article of manufacture having a metal wear surface which is relieved substantially uniformly throughout 15 to 60 per cent of its area to a depth of at least .0002 inch, said relieved and unrelieved areas of the wear surface having at least initially a continuous film thereon comprising fine or colloidal graphite bonded to the metal of the relieved and unrelieved areas by a phosphate of the metal.

14. An article of manufacture having a chromium wear surface provided with a plurality of relieved areas, said surface having at least initially a continuous film thereon extending into said areas and comprising fine or colloidal graphite bonded to the surface and areas by chromium phosphate.

15. An article of manufacture having a chromium wear surface provided with a plurality of relieved areas having a depth of at least .0002 inch, said surface having at least initially a continuous film thereon extending into said areas and comprising fine or colloidal graphite bonded to the surface and areas by chromium phosphate.

16. An article of manufacture selected from the group consisting of pistons and piston rings having a relieved wear surface coated at least initially with fine or colloidal graphite bonded to the surface by a phosphate of the metal thereof.

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