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2,311,653

# UNITED STATES PATENT OFFICE

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## TREATMENT OF FRICTIONAL SURFACES TO FACILITATE WEARING-IN

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No Drawing. Substituted for abandoned application Serial No. 93,920, August 1, 1936. This application August 7, 1939, Serial No. 288,834

8 Claims. (Cl. 148—6.5)

This invention relates to the treatment of metallic frictional surfaces of machine elements and especially to a treatment which prevents scuffing or seizing of moving mechanical elements in frictional contact during the breaking-in process.

Because of the increased power and increased speed of moving parts of recently designed automobiles, it has been found that formerly suitable lubricants are not capable of providing safe lubrication. This is especially true during the breaking-in process and in the case of cars provided with hypoid gears. Various lubricants have been developed in an effort to meet the extreme requirements necessary to insure absolutely safe lubrication under the high pressures and sliding friction encountered in modern machines.

The problem of lubricating hypoid gears has become particularly acute. Lubricants which have been provided for these gears can be classified into two general types, namely (1) corrosive extreme pressure lubricants containing, for instance, free sulfur or corrosive oil-soluble sulfur compounds, and (2) milder extreme pressure lubricants containing non-corrosive oil-soluble compounds of sulfur or other materials which eventually react with the metallic surface being lubricated to form a protective film which prevents scuffing or seizure. The significance of the term "non-corrosive extreme pressure lubricant" is in general well understood in the lubrication art. As an example of the line of division between corrosive and non-corrosive extreme pressure lubricants, such a lubricant of the sulfur-bearing type is regarded as corrosive if it darkens a polished copper strip immersed in the lubricant for one-half hour at 300° F., and is regarded as non-corrosive if no discoloration occurs under these conditions.

In testing gears and gear lubricants, we have found two characteristics to be generally true: first, that lubricants containing free sulfur or other distinctly corrosive materials used in corrosive extreme pressure lubricants allow new gears to be safely broken in under heavy loads with little danger of scuffing. However, such lubricants are not desirable for continued use after the gears have been "run-in" because of detrimental effects on bearings and other parts and because of accelerated wear produced on the gears. Of course detrimental action on bearings occurs to some extent even during breaking-in. Nevertheless, corrosive lubricants are being used because they have been regarded as essential.

The second effect which has been found to be true is that less corrosive extreme pressure lubricants, such as are satisfactory for well "run-in" gears, are not as desirable for use during the breaking-in period as are the more corrosive lubricants.

Thus the corrosive extreme pressure lubricants are more desirable than the non-corrosive because of increased film strength, but are less desirable because of corrosive action on bearings and because they produce an accelerated wear rate after continued use.

This invention avoids the above difficulties and provides a method of eliminating the necessity for highly corrosive extreme pressure lubricants, and in some cases the necessity of even mild or non-corrosive extreme pressure lubricants, during breaking-in of machine elements. The present invention also provides a method which facilitates running-in of closely fitting machine parts, such as piston rings and cylinder walls of internal combustion engines, where it is not feasible to use an extreme pressure lubricant.

Accordingly, an object of this invention is to eliminate the necessity of highly corrosive extreme pressure lubricants.

It is also an object of the invention to provide a process of treating gears and other mechanical elements, subject to metal-to-metal contact, so that danger of scuffing or seizing is avoided during the breaking-in process, even though non-corrosive lubricants are used and the raw gears or other elements are immediately run under conditions which would normally produce scuffing, such as heavy loads and high speeds.

Another object of the invention is to form by chemical action an integral thin tenacious coating on the teeth of gears prior to "running-in" and then to run-in such gears with a mild or non-corrosive extreme pressure lubricant.

A still further object of the invention is to provide an integral thin tenacious coating on the pistons, piston rings and/or cylinder walls of an internal combustion engine, by chemical reaction with the metal surfaces, whereby breaking-in of these parts is facilitated and scoring is avoided.

Metal surfaces may be treated according to our invention with the various reagents in a great number of ways to form reaction products with the metal surfaces and to give the desired action. It is obvious that in all cases strength of treating agent, temperature, the time of treatment,

should be adjusted so as to yield an integral, non-flaky, thin, tenacious film on the metal surfaces. The necessary conditions and adjustments are within the knowledge and are apparent to those skilled in the metal treating art. These conditions can be determined by simple tests.

It is also apparent that in the case of treatment of gears, either the entire gear or only the teeth thereof may be treated.

Three general types of treatment may be utilized:

(1) *Treatment with gases.*—As an example of this type, ferrous metal may be treated with hydrochloride acid vapors containing moisture.

(2) *Treatment with liquids.*—In this type of process, gears may be dipped, sprayed or painted with aqueous solutions of suitable water-soluble acids. Instead of the acids themselves, materials which will hydrolyze or decompose to give the free acid may be used. The treated metal is subsequently dried and when necessary, heated to effect chemical combination of the treating agent and the metal base. Likewise, the metal may be treated with colloidal suspensions of the acid or other suitable active ingredient. Where the treating agent is a liquid or can be melted at suitable temperatures the material itself in liquid phase may be utilized.

Treatment of ferrous metals with liquids may be combined with a tempering operation, as for instance by quenching in aqueous solutions of the treating acids. This combined treatment may be carried out in two steps: first, by quenching in the usual substantially inert liquids and second, while the metal is still hot from this tempering operation, treating to form a film as taught in the present specification.

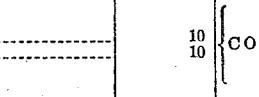
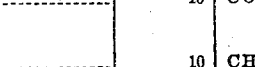
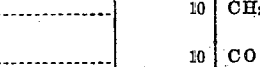
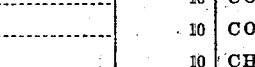
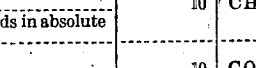
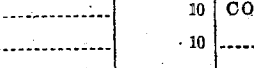
(3) *Treatment with solids.*—Another mode of operation is to dust the metal with a solid treating agent and produce chemical reaction by heating or by addition of small amounts of water to enable the acid to attack the metal.

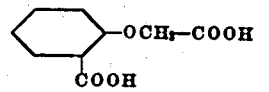
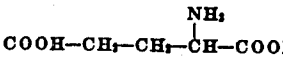
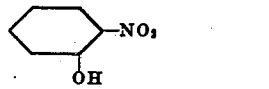
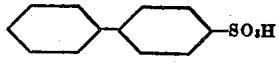
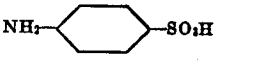
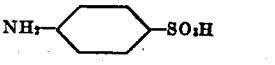
The preferred method of treatment consists in exposing ferrous metal surfaces to the action of aqueous solutions of various organic or chlorine containing acids. Varying periods of time are required, depending on the rate of reaction in each case. Temperatures of between 160 and 200° F. have been found to be most suitable.

To compare the utility of the films produced by the present invention, a testing machine of the type described in the S. A. E. Journal of December 1933, at page 402, was used. The steel cups used in this machine were washed and thoroughly cleaned in organic solvents. A bath of approximately 200 cc. of the acid solution (aqueous solutions were used unless otherwise indicated) was heated to a temperature of from 160° F. to about 200° F. and the steel cups to be treated were introduced for varying periods of time. In order to compensate for different reaction rates, the amount of reaction was usually estimated by the coloring produced on the metal and was permitted to proceed to about the same degree in each case. Where reaction rates were slow and of comparable rate, or where no coloring was produced, treatment was carried out for a given constant length of time.

A non-corrosive extreme pressure mineral oil lubricant containing a lead soap and sulfurized fatty oil was used for lubrication during the above tests. This lubricant alone carried a load of approximately 85 pounds on the untreated metal cups in the testing machine. The following table of experimental results shows the greatly increased load carrying capacity of the same lubricant after pretreatment of the frictional surfaces according to this invention.

*Load carrying capacities*

| Agent | Concentration weight per cent | Structural formula | Treatment | | Test cut at lbs. |
|---|---|---|---|---|---|
| | | | Average temp. | Duration | |
| UNTREATED SURFACE | | | | | |
| Hydroxy acids: | | | *Degrees F.* | *Minutes* | |
| Citric acid | 10 |  | 190 | 45 | [1] 540+ |
| Citric acid | 10 | | 180 | 16 | 510 |
| Tartaric acid | 10 | | 185 | 30 | 572 |
| Malic acid | 10 | | 170 | 10 | 452 |
| Lactic acid | 10 |  | 170 | 60 | 441 |
| Gluconic acid | 10 | | 185 | 15 | 418 |
| Unsubstituted acids: | | | | | |
| Succinic acid | 10 |  | 185 | 30 | 219 |
| Oxalic acid | 10 |  | 185 | 30 | 223 |
| Acetic acid | 10 |  | 185 | 30 | 215 |
| Cocoanut fatty acids in absolute alcohol (10%) | | | 170 | 135 | 132 |
| Unsaturated acid: | | | | | |
| Maleic acid | 10 |  | 165 | 10 | 564 |
| Miscellaneous: | | | | | |
| Tannic acid | 10 | | 170 | 16 | 286 |
| Pyruvic acid | 10 | | 172 | 15 | 175 |

| Agent | Concentration weight per cent | Structural formula | Treatment | | Test cut at lbs. |
|---|---|---|---|---|---|
| | | | Average temp. | Duration | |
| | | | *Degrees F.* | *Minutes* | |
| Salicylacetic acid | 5 |  | 178 | 60 | 263 |
| Nitrogen compounds: | | | | | |
| dl-Alanine | 10 | | 172 | 15 | 320 |
| d-Glutamic acid | 7 |  | 172 | 15 | 247 |
| Ortho nitrophenol | 1 |  | 175 | 70 | 255 |
| Sulphonic acids: | | | | | |
| Diphenylparasulphonic acid | 10 |  | 180 | 30 | [1] 550+ |
| Sulphanilic acid | 6 |  | 185 | 36 | 508 |
| Sulphanilic acid | 6 |  | 180 | 6 | 480 |
| Heavy petroleum sulphonic acid. | 10 | ---------- | 185 | 60 | 126 |
| Water-soluble petroleum sulphonic acid (average molecular wt.=250) | 10 | ---------- | 185 | 30 | 226 |
| Sulfur compounds: | | | | | |
| Thioglycolic acid | 10 | | 180 | 30 | [1] 580+ |
| Chlorine compounds: | | | | | |
| Trichloracetic acid | 10 | $CCl_3—COOH$ | 190 | 30 | [1] 540+ |
| Trichloracetic acid | 10 | $CCl_3—COOH$ | About 160 | 15 | 232 |
| Hydrochloric acid | 0.6N | HCl | 180 | 30 | [1] 548+ |

[1] Cups were not cut when machine automatically shut down at full load. Variations in shutdown load are due to difficulty in resetting controls on machine.

If a comparison be made between the results obtained by treatment with acetic acid (215 lbs.), lactic acid (441 lbs.) and thioglycolic acid (full load of the machine—more than 580 lbs.), all three of which are monobasic carboxylic acids, the first with no substituted groups, the second with a hydroxy group in the alpha position, and the third with a mercapto group in the same place, it is seen that the presence of the hydroxy group is extremely beneficial and that the closely related mercapto group is even more so. Two hydroxy groups are indicated to be more effective than one by comparing the results with tartaric acid (572 lbs.) and of malic acid (452 lbs.).

A comparison of lactic acid, dl-alanine, and pyruvic acid shows that, when substituted in the alpha position of a mono-basic straight chain acid, the order of decreasing effectiveness of substituents is hydroxy, amino, and keto groups.

The unsaturated carbons adjacent to the carboxyl groups in maleic acid (564 lbs.) show a highly beneficial effect when compared with results obtained from succinic acid (219 lbs.).

Chlorine is an effective substituent in acids as shown by increase in load carrying capacity of trichloracetic acid (540 lbs.) over that of acetic acid (215 lbs.). Hydrochloric acid itself is extremely effective even though the film produced is theoretically water-soluble. Apparently a portion of the metal chloride formed by this acid is retained tenaciously on the metal surface.

The heavy petroleum sulfonic acids used in the tests indicated are easily dispersible in water but are not truly soluble therein as shown by the fact that these acids impart some cloudiness to the water. The water-soluble petroleum sulfonic acids dissolve to give clear water solutions. Comparison of the above two acids shows the water-soluble ones to be much more effective for the purposes of this invention. Likewise, comparison of the effectiveness of cocoanut oil fatty acids (132 lbs.) which are water-insoluble and acetic acid (215 lbs.) or succinic acid (219 lbs.) shows that the most effective reagents are water-soluble.

It is evident from the above presented facts that when steel surfaces are treated with water-soluble organic or chlorine-containing acids increased load carrying capacities are obtained. Mono- and poly-basic acids, both saturated and unsaturated, unsubstituted and substituted with either mercapto, hydroxy, amino, keto, or halogen substituents; substituted aromatic acids, substituted and unsubstituted aromatic sulfonic acids, and substituted phenols, comprise effective treating agents.

It is also apparent from the above disclosure that there are many acids within the scope of our invention which have sufficient activity to attack the metal surface to be treated and to form thereon the required integral tenacious adherent film.

When treating case-hardened metals, the treatment should be controlled so that only a portion of the hardened encasing metal is attacked by our reagents. The remaining portion of the hardened metal is then retained and there is no substantial alteration in the hardness of the underlying metal surface of the treated article.

While the invention provides a means for running-in new gears with non-corrosive extreme

pressure lubricants, it is also applicable to use with extreme pressure lubricants that are mildly corrosive. For conditions of operation in which very active or corrosive extreme pressure lubricants have heretofore been required to prevent scuffing during running-in, less corrosive extreme pressure lubricants may be rendered usable and satisfactory by pre-treating the frictional surface as herein described. For example, corrosive extreme pressure lubricants containing up to 1% free sulfur have heretofore been found inadequate to prevent scuffing of gears under certain breaking-in conditions. This same lubricant prevents such scuffing under the same conditions when used with gears pretreated according to this invention.

While in many cases the film formed by our pretreatment is eventually removed by wear, tests have shown that the scoring of new frictional surfaces generally occurs in the early stages of use, particularly when heavily loaded. Our pretreatments provide a protecting film which is resistant to extreme pressures, and which prevents scoring or seizing during this initial critical period. Consequently our invention also has utility for breaking-in machine elements where the object is merely to insure proper wearing-in of the parts and it is not necessary or desirable to use extreme pressure lubricants. Accordingly the pretreatment described in this invention is applicable to piston rings and/or cylinder liners of internal combustion engines and when applied thereto facilitates breaking-in of a new motor.

The phenamenon responsible for the surprising results obtained by combining our pretreatment with the use of non-corrosive extreme pressure lubricants may be a catalytic one. The preformed films themselves are worn off in use by friction. However, these preformed films seem to act as a catalyst and facilitate reforming of a new film by the non-corrosive extreme pressure lubricant as soon as parts of the old film are worn off. In the absence of these preformed films, the non-corrosive extreme pressure lubricants are less efficient in preventing scuffing and seizing during running-in of metal parts, presumably because initial formation of the film takes place more slowly. Irrespective of the above catalytic theory, which is not regarded as essential to the invention, we have discovered a physical effect resulting from a particular combination of process steps which greatly facilitates lubrication of hypoid gears and other mechanical elements where ferrous metal to ferrous metal frictional contact under high pressures is involved.

The generic term "organic acids" is used in the claims to include carbon-containing acids having two or more carbon atoms in the molecule. The acidic group of the acid may be one of various types, such as the carboxylic, phenolic or sulphonic groups herein disclosed. Also, substituted organic acids containing elements other than carbon, hydrogen and oxygen have been disclosed and are encompassed within the generic scope of the invention and within the scope of the term "organic acids."

This application is substituted for our application Serial No. 93,920, filed August 1, 1936.

The scope of the invention is not limited to the specific examples of the present specification but includes numerous variations and alterations within the spirit and scope of the appended claims.

We claim:

1. In a process of breaking-in machine elements having ferrous metal bearing surfaces subject to friction, which comprises lubricating said surfaces with a lubricant having an extreme pressure film strength inadequate to insure against scoring or scuffing, the step of pretreating and converting the metal of at least one of said elements to a non-metallic compound by reacting therewith a water-soluble organic sulfonic acid to form thereon an integral, thin non-metallic film whereby scuffing or scoring is prevented.

2. A process as in claim 1, in which the sulfonic acid is an aromatic sulfonic acid.

3. An article of manufacture comprising a machine element having a ferrous metal frictional bearing surface and selected from the group consisting of pistons, piston rings, and cylinder liners, the frictional bearing surfaces of said elements having thereon an integral, thin non-metallic film comprising the reaction products of the metallic surface and a water-soluble chlorine-containing organic acid.

4. A process which comprises treating a machine element having a ferrous metal frictional bearing surface and selected from the group consisting of pistons, piston rings, and cylinder liners, by reacting the metal of said surface with a chlorine-containing organic acid capable of forming an integral, thin film of non-metallic reaction products and thereby facilitating wearing-in of said parts.

5. In a process of breaking-in machine elements having ferrous metal bearing surfaces subject to friction, which comprises lubricating said bearing surfaces with a lubricant having an extreme pressure film strength inadequate to insure against scoring or scuffing, the step of pretreating and converting the metal of at least one of the frictional bearing surfaces of said elements to a non-metallic compound by reacting therewith a water-soluble chlorine-containing organic acid having chlorine substituted on an alpha carbon atom and forming thereon an integral, thin non-metallic film whereby scuffing or scoring is prevented.

6. The process of preventing scuffing and scoring between ferrous metal bearing surfaces under extreme pressures comprising pretreating said surfaces, after machining to final dimensions but prior to use, with a water-soluble organic acid by chemically reacting said acid with the ferrous metal bearing surfaces to form thereon an integral, thin lubricating film, lubricating said surfaces with a mineral lubricant, and subjecting said surfaces to frictional contact under extreme pressure.

7. The process of preventing scuffing and scoring between ferrous metal bearing surfaces under extreme pressures comprising pretreating said surfaces, after machining to final dimensions but prior to use, with a water-soluble substituted organic acid selected from the group consisting of mercapto, hydroxy, amino, keto and chloro organic acids by chemically reacting said acid with the ferrous metal bearing surfaces to form thereon an integral, thin lubricating film, lubricating said surfaces with a mineral lubricant, and subjecting said surfaces to frictional contact under extreme pressure.

8. A process of improving the load carrying capacity of a machine element having a ferrous metal frictional bearing surface machined to final dimensions and normally subjected to lubrication under service conditions ordinarily tending to

cause scuffing and scoring of said surface, said process comprising chemically treating, prior to use, said ferrous metal frictional surface with a water-soluble organic acid selected from the group consisting of mercapto, hydroxy, amino, keto and chloro organic acids by chemically reacting said acid with said surface to form an integral non-metallic film thereon, and lubricating said surface with an oil lubricant while subjecting said surface to frictional contact.

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CERTIFICATE OF CORRECTION.

Patent No. 2,311,653. February 23, 1943.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, in the table, last column thereof, under the heading "Test cut at lbs." and on the line with "UNTREATED SURFACE" insert the numeral --85--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of June, A. D. 1943.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)