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DRY LUBRICATION

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The present invention relates to improvements in dry-lubricating. In particular, the invention relates to articles intended to be subjected to a frictional strain and having improved permanent self-lubricating properties, to a process for making said articles, to a novel dry-lubricating process and to a novel lubricating agent.

Besides the large number of lubricant liquids which are already known to the art lubricant solids which commend themselves by their special structural character (laminar lattice) have become increasingly popular in recent years. In some applications they offer decisive advantages over lubricant oils. The coefficient of friction of these substances is, for instance, much less affected by temperature changes than that of lubricating oils so that they assure the maintenance of constant lubricant properties within a wide temperature range.

The most common solid lubricants of laminar structure hitherto used are more especially molybdenum disulphide and graphite.

I have now discovered that fluorinated graphite constitutes a lubricant having outstanding dry-lubricating properties which in many respects is superior to the dry-lubricants which have been known in the art.

It is an object of this invention to provide a novel dry-lubricating agent useful for imparting permanent self-lubricating properties to various articles having working surfaces intended to be subjected to a frictional strain.

Another object of this invention is to provide an article having a working surface intended to be subjected to a frictional strain, which surface has outstanding permanent self-lubricating properties.

A further object of the present invention is to provide a simple and economic process for dry-lubricating articles having working surfaces intended to be subjected to a frictional strain.

According to this invention an article having a working surface intended to be subjected to a frictional strain is provided, wherein said working surface comprises fluorinated graphite as a lubricant.

According to another feature of this invention a process for making said article is provided which comprises providing the working surface of said article with fluorinated graphite as a lubricant.

The article to which self-lubricating properties are imparted according to this invention may consist of any material capable of withstanding a long-lasting frictional strain, such as a metal, a metal base alloy, a plastic material, glass, a fritted material, a precious or semi-precious stone and the like. The article can be a part intended to be used in machinery, instruments, clocks and watches, and the like.

According to one embodiment of the present invention fluorinated graphite is applied in the form of an adhering film of preferably less than 1 micron thickness and more especially less than 0.0005 mm. thickness, to at least the frictionally engaging surfaces of parts such as those used in watches and clocks of all kinds, and especially of the springs in clocks and watches for the purpose of providing lasting films which will impart self-lubricating properties of these parts.

Parts of clocks and watches provided with a thin coating of the described kind which firmly adheres to the

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friction surface require no further lubrication by means of an oil or a grease, so that they can be built ungreased and unoled into the case of a watch or a clock and yet do not exhibit the drawbacks associated with unlubricated parts consisting of like materials or of lubricated parts when the lubricant ages.

The term fluorinated graphite describes a substance obtained for instance by exposing graphite to a current of fluorine. In certain respects the structure of this fluorinated graphite is probably similar to that of molybdenum disulphide.

Fluorinated graphite can be prepared e.g. as follows:

The fluorination of graphite for producing fluorinated graphite may be performed by methods which are already known—for instance as described by C. Ruff and G. Bretschneider, in *Z. anorg. allg. Chem.* 217, 1 (1934), and by W. and O. Rüdorff, in *Z. anorg. allg. Chem.* 253, 281 (1947). Before the reaction is started, a stream of fluorine is conducted over the graphite for an hour at room temperature at the rate of several litres per hour for the purpose of expelling the air from the apparatus as completely as possible. The gas, before entering the reaction vessel, is taken through a copper trap cooled by liquid oxygen for removing hydrofluoric acid. In the course of approximately another hour the graphite is heated to reaction temperature, generally between 400 and 500° C. The fluorination is continued for several hours, and then the reaction is interrupted and the reaction product allowed to cool in the fluorine current. The probable formula CF has been ascribed to the fluorinated graphite obtained in this way.

Compared with the other solid lubricants referred to above, fluorinated graphite offers important advantages. Its production by comparison with that of polyfluorocarbon or with the process of purifying molybdenum disulphide to serve as a lubricant is simple and inexpensive. Compared with graphite and with polyfluorocarbon, it has the further advantage of exhibiting an exceptionally satisfactory adhesion to a wide variety of solids, such as metals, a property which may be due to its structure, i.e. the parallel alignment of its dipoles.

Fluorinated graphite may be applied in various ways to the surface of an object which is to be subjected to friction. Experiments have shown that several methods are available. It was found for instance that ordinary mechanical application, for instance by dusting or rubbing a part of or all of the surfaces in question with fluorinated graphite, produces an effective and durable lubricant film on the surfaces that have been thus treated. For example, by rubbing fluorinated graphite of the composition CF_{0.93} on a small plate of iron a lubricant film was obtained which, upon being tested with a steel pin, was found to have a coefficient of friction of only 0.07 to 0.12, whereas untreated iron plates tested with the same pin has a coefficient of friction of 0.26 to 0.28.

An alternative method of applying the fluorinated graphite to a surface consists in suspending the same in inert liquids, such as water or organic liquids, and in applying the resultant dispersion to the surface in question. A lubricant film will then remain on the surface when the liquid evaporates. In this manner porous objects such as sintered metals can be successfully impregnated with fluorinated graphite. The part which is to be provided with a lubricant film may also be dipped into a suspension of an inert liquid and fluorinated graphite having a carbon to fluorine ratio of about 1:1 and the suspension with the part immersed therein exposed to ultrasonic vibrations. Thereafter the heated article is removed from the suspension and the adhering inert liquid is removed.

Another method which is of special practical interest

is the production of compact bodies, for instance of metal, plastic, and so forth, by incorporating a certain quantity of fluorinated graphite therein in the course of their actual production. In such a case the lubricant film which forms when such bodies are in frictional contact will renew itself at any point where it has been destroyed by abrasion. However, in the production of such bodies which contain the fluorinated graphite care must be taken to see that the temperature at which the fluorinated graphite decomposes will not be exceeded. Consequently the metals employed for making such parts should be of a kind that sinter to form compact bodies at temperatures below the decomposition temperature of the fluorinated graphite. Such metals include for instance copper, gold, bronze, brass, titanium, aluminum and nickel. An illustrative example is a bronze containing 90% copper and 10% tin intimately mixed in powder form with 2% fluorinated graphite and then hot pressed for 30 seconds in a heated die at 400° C. with the application of 6 tons/sq. cm. pressure. The coefficient of friction measured between a chromium plated steel pin in frictional engagement with the polished surfaces of such a bronze body was roughly 0.12. It will be readily understood that the percentage addition of fluorinated graphite may be varied within very wide limits, though for reasons of economy the addition naturally will be as small as possible. A further method of forming a self-lubricating article comprises adding fluorinated graphite having a carbon to fluorine ratio of 1:1 in powder form to a granular material of which the article is to be made, and then sintering the mixture at a temperature below 500° C. The resulting article will have fluorinated graphite impregnated therein in an amount sufficient so that the working surfaces will be self-lubricating when subjected to frictional strain.

Although in the preceding description reference is made principally to the application of fluorinated graphite in the case of metals, it is not intended that the invention should be limited in scope to metal parts containing fluorinated graphite or provided with a film of fluorinated graphite, since equally satisfactory results can be obtained by providing synthetic resin plastics, precious and semi-precious stones, e.g. rubies, sapphires, or glass parts, which have surfaces which will be exposed to frictional wear, with lubricant or sliding films of fluorinated graphite.

The articles contemplated by the invention may be for various applications; for instance they may be parts of machinery, parts of instruments, clocks and watches, and so forth. Good results have been achieved principally in the case of parts for clocks and watches, such as watch springs, especially main springs, parts of the escapement, arbors, pivot pins, bearings and the like.

In the case of watch springs the very small film thickness which can be achieved with fluorinated graphite calls for the provision of less space in the barrel than that occupied by springs lubricated in the conventional manner. Watch springs lubricated with a film of fluorinated graphite unwind evenly and uniformly and the convolutions of the spring will not stick together even after prolonged service. The conditions of the lubrication are also better and the available moment of power is higher. The springs may therefore be thinner and of greater length, so that the rate of decrease of torque is less when the spring unwinds, and the spring is capable of storing a greater amount of reserve power. Moreover—in contradistinction to conventional springs—springs according to the invention are adequately lubricated for the rest of their life and therefore require no maintenance. No lubrication of the spring with grease or oil during assembly is needed, a factor which contributes to reducing the cost of assembly.

All the tests and experiments that have been carried out confirm that a relatively thin film of fluorinated

graphite exhibits a remarkably tenacious adhesion to metal surfaces, and that it fully satisfies the needs of producing a practically enduring lubricant and/or sliding effect between slidably contacting bodies of different composition.

It is not intended to limit the invention to the specific embodiments described hereinbefore since various modifications may be used in carrying out the invention as will be obvious to those skilled in the art.

What I claim is:

1. A method of using fluorinated graphite having a carbon to fluorine ratio of about 1:1, comprising applying it to a surface which is subjected to a frictional strain for lubricating said surface.

2. A method as claimed in claim 1 in which said fluorinated graphite is applied over only a part of said surface.

3. A method as claimed in claim 1 in which said fluorinated graphite is applied over the whole of said surface.

4. A method as claimed in claim 1 in which said fluorinated graphite is applied to a thickness of not more than ½ micron.

5. A dry lubricating method comprising the step of coating a surface which is to be subjected to a frictional strain with fluorinated graphite having a carbon to fluorine ratio of 1:1.

6. A process according to claim 5, wherein the fluorinated graphite having a carbon to fluorine ratio of about 1:1 is applied to said working surface in the form of a suspension in an inert liquid and the liquid phase is removed so as to leave a coating of the fluorinated graphite having a carbon to fluorine ratio of about 1:1 at least partially covering said working surface.

7. A process according to claim 5, wherein said working surface is immersed in a suspension of fluorinated graphite having a carbon to fluorine ratio of about 1:1 in an inert liquid, the suspension and said working surface immersed therein are subjected to the action of ultrasonic vibrations, the treated article is removed from the suspension, and the adhering inert liquid is removed.

8. A process as claimed in claim 5, wherein the fluorinated graphite having a carbon to fluorine ratio of about 1:1 is brought into contact with the surface during its manufacture so that at least that portion of the surface which is to be subjected to a frictional strain incorporates fluorinated graphite having a carbon to fluorine ratio of 1:1.

9. A process for making a self-lubricating article from sintered material and having a working surface intended to be subject to a frictional strain, comprising adding fluorinated graphite having a carbon to fluorine ratio of about 1:1 in powdered form to the granular material of which the article is to be made and sintering the mixture at a temperature below 500° C.

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