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ETCHED FILLER CONTAINING POLYTETRAFLUOROETHYLENE BEARING MATERIAL

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This invention relates to polytetrafluoroethylene and more particularly to polytetrafluoroethylene containing fillers which impart improved properties to the polymer without impairing other of its properties.

It has long been known that polytetrafluoroethylene has certain desirable properties which make it particularly suitable for forming various devices, such as bearings, where relative motion of two contacting surfaces is involved. Polytetrafluoroethylene has been found particularly well adapted to such uses where normal lubricants are either ineffective or undesirable.

The adaptability of polytetrafluoroethylene to such uses is due primarily to the fact that it has a very low coefficient of friction. However, it possesses one major drawback in that it also shows poor wearing properties and load-bearing characteristics. In order to take advantage of the low coefficient of friction of this polymer and at the same time to modify it to improve its wearing properties, it has been suggested that various fillers be incorporated in the polytetrafluoroethylene. These fillers work not only to improve the wearing characteristics of the polymer, but they serve also as a reinforcing medium advantageous to the performance of the polymer under certain conditions. However, these fillers usually increase the coefficient of friction of the modified polytetrafluoroethylene thus obviating, to at least some extent, the advantage of adding them.

It would therefore be desirable to have a modified polytetrafluoroethylene, i.e., one containing a filler, which would retain the low coefficient of friction characteristic of the original polymer and at the same time materially improve its wearing properties. It would also be desirable to provide a modified polytetrafluoroethylene, and a process for making it, which would permit the controlling of the coefficient of friction of the modified material permitting, for example, one portion of the modified surface to be made slippery or self-lubricating while another portion is maintained relatively nonslippery.

It is therefore a primary object of this invention to provide a modified polytetrafluoroethylene, and more particularly a modified polytetrafluoroethylene surface, suitable for anti-friction devices which retain the low coefficient of friction associated with polytetrafluoroethylene surfaces and at the same time exhibits a very marked improvement in wearing properties over those normally associated with polytetrafluoroethylene surfaces.

It is another object of this invention to provide a modified polytetrafluoroethylene which when formulated in accordance with this invention will assume certain additional desirable characteristics without detracting from the desirable properties already inherent in polytetrafluoroethylene. Another object is to provide the surface of a polytetrafluoroethylene modified with filler which may be treated to render only a portion of that surface

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self-lubricating or to provide an article having surfaces of different characteristics. Still another object is to provide a modified polytetrafluoroethylene which possesses improved characteristics which are not attained at the expense of the impairment of the normally desirable properties of polytetrafluoroethylene.

The modified polytetrafluoroethylene product of this invention is made by formulating the polytetrafluoroethylene with a suitable filler, such as glass fibers, carbon, copper, molybdenum sulfide and the like, and subsequently removing or etching away a portion of the filler exposed at the surface to give the surface certain desired properties while maintaining the bulk properties characteristic of the filled polymer. For example, by etching the surface of polytetrafluoroethylene containing glass fibers with hydrofluoric acid for a relatively short period of time, it is possible to retain the natural low coefficient of friction associated with the pure polymer and at the same time maintain the superior wearing and mechanical properties of the filled material.

Although it is not known exactly why the removal of a small portion of the filler from the surface of a filled polytetrafluoroethylene material imparts marked improvements in its properties, it may be possible to explain the unexpected and highly desirable results in the following manner. In etching out a small portion of the filler, the polytetrafluoroethylene portion remaining to form the uppermost surface apparently extends above the substructure of the unreacted polytetrafluoroethylene-filler composition to exert some beneficial thermal effect which takes advantage of the extremely high coefficient of expansion of the polymer. In any event, when bearing surfaces or other anti-friction surfaces, formed of polytetrafluoroethylene and a filler treated in the manner of this invention, are exposed to extended friction and wear tests they exhibit the low coefficient of friction of pure polytetrafluoroethylene, but they no longer exhibit the rapid wear and flaking which have come to be associated with unmodified polymer bearing surfaces.

The fillers which may be added to polytetrafluoroethylene are those which are generally known in the art and include, but are not necessarily limited to, glass fibers, copper, bronze, carbon and graphite, molybdenum sulfide, lead, clay, talc, asbestos, silica, coke flour, calcium fluoride and any other finely comminuted solids which are compatible with polytetrafluoroethylene and at least one of which can be removed by the etching step without effect on the polytetrafluoroethylene. These fillers may be introduced into the polytetrafluoroethylene to give a final product, before surface etching, ranging from 10 to 50 percent filler by volume of the total polytetrafluoroethylene filler composition.

The techniques of introducing these fillers into polytetrafluoroethylene are well known in the art. One such method is to coagulate the filler and the polytetrafluoroethylene in a dispersion. The mixture thus formed, after proper agitation and mixing, is filtered and washed (several times if necessary) dried and heated to about 575° F. Alternatively, polytetrafluoroethylene may be pulverized at low temperatures (liquid nitrogen) and the pulverized powder uniformly mixed with the filler in powder form. Or, a molding powder prepared, for example by coagulating a polytetrafluoroethylene emulsion, can be mixed with the filler.

The resulting polytetrafluoroethylene-filler mixture, in which the polytetrafluoroethylene and filler are uniformly mixed together, is then pressure-molded, the amount of pressure depending usually upon the amount of filler added. For example, 2,000 p.s.i. may be employed where the filler is present in a range from 10 to 15 percent by volume, while as much as 10,000 p.s.i. may be used where the filler is present up to 50 percent by volume. The resulting molded article is then baked or sintered in an oven or in a fluid bath at temperatures about 700° F. or somewhat higher.

In the preparation of bearing tape material, it is common to mold cylindrical shapes in the manner described above and then skive this into tape. Filled polytetrafluoroethylene tape made in the manner described above is then treated in accordance with this invention to impart improved characteristics to the tape and to form filled polytetrafluoroethylene bearings having improved characteristics. Among these improved characteristics are low coefficients of friction and lower operating temperatures which in turn impart improved load-bearing characteristics to the bearings formed.

The agent or agents used to etch the surface of the filled polytetrafluoroethylene to remove a small amount of the filler from the surface depends upon the filler used. Materials suitable for etching should be those which will react with the filler, but not with the polytetrafluoroethylene (at least under the conditions imposed in the treatment), to produce a product or products which are removable from the surface either as a solution or by subsequent treatment such as washing, etc. Preferably the etching material is one in which the filler is readily soluble. Thus, for example, it has been found that hydrofluoric acid is a more satisfactory etchant for glass fibers in the polytetrafluoroethylene than is strong caustic. Copper-filled polytetrafluoroethylene may be surface treated with nitric acid, and carbon-filled polytetrafluoroethylene with Caro's acid. The action of the etching agent may be stopped by any suitable method such as neutralization, washing, etc. The low friction surface thus created is reinforced by the underlying sub-structure of the polytetrafluoroethylene-filler composition.

Etching may be accomplished by any convenient and suitable method, such as by fully immersing the tape to be etched in the etching liquid. In this method both surfaces of the polytetrafluoroethylene are etched. Another way of etching comprises exposing one or a portion of both surfaces of the filled polytetrafluoroethylene tape to a liquid or to etching vapors such as for example hydrofluoric gas in the case of the glass-filled material.

It would be very difficult to express the amount of etching in linear dimensions; rather it is to be described in terms of the change occurring in the surface character, the amount of time during which the surface is exposed to the etching material, and the wearing characteristics of the finally created surface. Conceivably, it would only be necessary to remove sufficient filler to leave polytetrafluoroethylene ridges which are no more than one to two molecules high. Practically, this is not easy to accomplish or measure, and the optimum etching time for any filler used must finally be determined experimentally to achieve a desired combination of properties for the surface. In general, it may be said that the longer the etching is carried out, and hence the deeper the pitting which results through the removal of more filler, the closer the surface will take on the properties of polytetrafluoroethylene. In fact it has been found that once sufficient etching has been accomplished further exposure of the filled polytetrafluoroethylene to the etching material is not required. Thus, for example, in the case of polytetrafluoroethylene filled with glass fibers, it is preferable to etch with hydrofluoric acid for a period from about two to five minutes. Etching times up to 30 minutes are possible and the resulting modified polytetrafluoroethylene possesses good characteristics, but the polytetrafluoroethylene does not ex-

hibit any better load-bearing characteristics than when the etching time is accomplished in about five minutes.

It is possible in the etching process that that portion of the filler which is exposed to the etching material is not completely removed but rather is partially removed and partially modified in situ. Thus, for example, it would appear feasible to postulate that in the case of treating a polytetrafluoroethylene-glass fiber surface with hydrofluoric acid it would be the silica portion of the glass which would be primarily attacked and that possibly the other glass components, particularly oxides or perhaps even fluorides of sodium, potassium and the like remained, if not on the surface, closely below it in the minute depressions formed in the etching process.

When a polytetrafluoroethylene surface containing glass fibers is etched in accordance with the process of this invention, it is changed from a rough (even almost abrasive) surface to one which is visibly slightly pitted but which has a very smooth, wax-like surface to the touch.

A number of filled polytetrafluoroethylene tapes suitable for testing as bearing materials were made up and the filler etched out in accordance with this invention. The examples given below, which are meant to be illustrative and not limiting, are included to further describe this invention and to show the improvement achieved in terms of lowered coefficients of friction and operating temperatures compared with untreated filled polytetrafluoroethylene. Performances of ordinary filled polytetrafluoroethylene and of filled polytetrafluoroethylene etched in accordance with this invention as bearing materials were evaluated in a bearing test machine. This test machine is, of course, not a part of this invention but it is described briefly herewith.

Two test shafts, each one consisting of an eight-inch length of one-inch diameter shaft supported in a pair of heavy-duty ball bearing pillow blocks were used. These shafts were belt-driven on one side of the pillow blocks, while the test positions were provided by an overhang on the opposite side of the pillow blocks. This design made it very easy to interchange test bearings and also facilitated measurement of shaft center line temperature under the bearing.

One of the test shafts was driven by a speed controller which permitted continuous adjustment from 0 to 3600 r.p.m. The other shaft was belt driven from a conventional 1750 r.p.m. motor. A selection of pulleys permitted a variety of speeds in the range of 600 to 2000 r.p.m. The adjustable speed shaft was used for detailed measurements, while the second shaft was used primarily for wear tests.

The tester utilized a free-floating bearing holder from which bearing torque measurements could be taken. The bearing torque was transmitted to a cantilevered beam by an arm on the bearing holder. A strain gauge bridge on the cantilevered beam provided the means for measuring beam deflection which is proportional to the bearing torque. A screw at the end of the holder arm allowed the holder to be kept level. A dial indicator riding against the holder was used as the zero reference point during levelling.

The bearings to be tested were cut from 1-inch wide tape and placed in an insert which, in turn, was placed in the steel bearing holder. Brass end plates were used to retain the bearing in the insert. Loading was applied to the bearing holder through a spherical bearing suspension system using dead weights to 40 pounds and an air cylinder to about 600 pounds.

Two thermocouples were installed in each bearing holder, one in a well in the bearing holder itself, the other in a well bored into the center of the shaft and extending to about the midpoint of the bearing surface. The shaft well temperature was usually recorded, along with the torque measurement from the strain gauge. Running time meters were provided to record bearing life.

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The following examples, which are meant to be illustrative and not limiting, will indicate the order and range of etching time which have been found desirable for a variety of fillers. They will also indicate the unexpected and greatly improved performance achieved by the modified filled Teflon surfaces of this invention.

EXAMPLE I

Glass-filled polytetrafluoroethylene containing 25 percent glass fibers by volume was made up by mixing the powdered Teflon and glass fibers by a known method as described above. Cylindrical molds were formed from this mixture and tape of approximately 0.030 inch thickness was skived from this mold. Samples of this tape were immersed in concentrated hydrofluoric acid for 2, 5, 15 and 30 minutes at room temperature. After being etched in this manner the tape was washed with water and dried. Test bearings were cut from these etched samples and placed in the bearing test machine described above. Inasmuch as times above 5 minutes did not materially change or improve the load-bearing characteristics of the bearing thus formed, performance data for the 5-minute etched filled polytetrafluoroethylene are given below. These performances can be considered representative of polytetrafluoroethylene bearing material containing glass fibers, the surface of which has been etched.

Bearing-Test Evaluation of Glass-Filled Polytetrafluoroethylene Tape Unetched and Etched

[75% polytetrafluoroethylene; 25% glass fibers by volume]

Load P (lbs.)	Velocity V (ft./min.)	PV	Unetched Glass-Filled Polytetrafluoroethylene		H ₂ F ₂ Etched Glass-Filled Polytetrafluoroethylene	
			Max. Coeff. Friction	Max. Temp., °F.	Coeff. of Friction ¹	Max. Temp., °F.
70-----	1800	33,000	0.50	900	-----	-----
40-----	1700	18,000	-----	-----	0.2	225
200-----	900	47,000	0.25	850	-----	-----
40-----	900	9,000	0.60	550	-----	-----
171-----	400	18,000	-----	-----	0.2	280
143-----	400	19,000	-----	-----	0.2	230
135-----	250	9,000	0.45	450	-----	-----
143-----	200	7,500	-----	-----	0.2	180

¹ Figures for coefficients of friction for the etched samples represent highest values found.

Although controls, i.e., filled polytetrafluoroethylene which had not been etched, are not available on a strictly comparable basis to be compared with the etched bearing material, it will be seen from the above tabulation that the coefficients of friction of the etched tape remained markedly and consistently lower than the coefficients of friction of the unetched tape. The maximum temperatures recorded for the bearings of the etched material (tested under the conditions given) were always very much lower than temperatures recorded for the unetched bearings.

In the case of any plastic-type bearing of which the filled polytetrafluoroethylene bearings of this invention are an example, the reduction in temperature of operation is particularly important for it means that the bearing life is considerably extended and that the load-bearing characteristics of the bearing, which are a function of temperature, are much improved. Thus, by the process of this invention it is possible to take advantage of the inherent low coefficients of friction associated with unfilled polytetrafluoroethylene and the high load-bearing characteristics of the filled polytetrafluoroethylene. This means that bearings prepared in accordance with the process of this invention surpass the performance of either unfilled polytetrafluoroethylene or unetched polytetrafluoroethylene.

EXAMPLE II

Samples of polytetrafluoroethylene tape filled with 15 and 25 percent copper powder by volume were made up in the manner described in Example I. In this case the

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copper powder was etched by immersing the filled tape in concentrated nitric acid for about 60 minutes. The resulting etched copper-filled polytetrafluoroethylene tape was evaluated in the bearing test machine described above. The results are tabulated below for the 25%-copper compositions. Comparable results were obtained for the 15%-copper compositions.

Bearing-Test Evaluation of Copper-Filled Polytetrafluoroethylene Tape Unetched and Etched

[75% polytetrafluoroethylene; 25% copper powder by volume]

Sliding Speed (ft./min.)	Coefficient of Friction	
	Unetched Copper-Filled Polytetrafluoroethylene	HNO ₃ -Etched Copper-Filled Polytetrafluoroethylene
0-----	0.11 to 0.17	0.05 to 0.09
13-----	0.20	0.10
26-----	0.19	0.20
78-----	0.18	0.17

It was found that at slow sliding speeds the bearing tape prepared by etching out the copper in the surface gave much lower coefficients of friction than the unetched tape. At higher speeds, the etching did not seem to have any measurable influence. However, since it is fairly common to employ plastic-type bearings, and especially polytetrafluoroethylene bearings, at low speeds it will be seen that the etching of the surface does contribute to the performance of the copper-filled polytetrafluoroethylene bearings.

A number of modifications in the process of this invention will occur to those skilled in the art. Thus, for example, it may be preferable to etch the filled polytetrafluoroethylene surface in a pattern or to etch but one side of the bearing surface. Likewise, it may be desirable to form perforated bearings, the perforations being made before or after etching.

The data presented in the examples clearly indicates the unexpected major improvements imparted to filled polytetrafluoroethylene characteristics by etching away a minor portion of the filler from the surface of the material. These improvements are particularly marked with respect to lowered coefficients of friction and lower bearing running temperatures. Thus by the process of this invention it is possible to prolong the life of filled polytetrafluoroethylene bearings and to use modified polytetrafluoroethylene in bearing applications heretofore not considered as suitable because of the low load-bearing characteristics of the unmodified (unetched) filled polytetrafluoroethylene.

We claim:

1. As a new article of manufacture a bearing material formed of a matrix of polytetrafluoroethylene containing from about 10 to 50% by volume of a fine particulate inorganic filler having the surface thereof etched to provide pits no deeper than the smallest dimension of said filler, said pits having ridges of said polytetrafluoroethylene no greater than a few molecules high.

2. Article in accordance with claim 1 wherein said filler is glass fibers.

3. Article in accordance with claim 1 wherein said filler is copper powder.

4. Method of forming an article suitable for use in construction of bearings exhibiting a low coefficient of friction in conjunction with good wearing properties and load-bearing characteristics, comprising the steps of

(a) uniformly incorporating into polytetrafluoroethylene a fine particulate inorganic filler in an amount equivalent to between about 10 and 50% by volume of the mixture thus formed;

(b) shaping said mixture into an article of a desired configuration thereby forming a matrix of said polytetrafluoroethylene containing said filler; and

- (c) treating the surface of said article with a substance destructively reactive with said filler and inert toward said polytetrafluoroethylene under the conditions of treatment at a temperature and for a time sufficient to form pits no deeper than the smallest dimension of said filler in said surface, said pits having ridges of said polytetrafluoroethylene no greater than a few molecules high.
5. Method in accordance with claim 4 wherein said filler is glass fibers and said treating comprises etching with hydrofluoric acid.
6. Method in accordance with claim 4 wherein said filler is copper powder and said treating comprises etching with nitric acid.

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