This invention relates to a process for applying a lubricant to polytetrafluoroethylene in particulate form, to produce a free-flowing paste which can be extruded or otherwise compressed into various forms or shapes.

It has been known that polymers in general can be extruded more readily by coating particles thereof with a lubricant. In the case of polytetrafluoroethylene, incorporation of such lubricants has been unusually troublesome and various devices and methods have been employed to convert granular and powdery forms of polytetrafluoroethylene to material which could be readily molded or otherwise shaped. The Lontz and Robb Patent, U. S. 2,593,582, describes a process for incorporating lubricants into polytetrafluoroethylene by contacting dry colloidal polymer particles with an atmosphere comprising a mist of thickened saturated hydrocarbon having a boiling point of from 220° to 400° C. at atmospheric pressure. Equipment for coating particulate solids with liquid coatings has been employed in various arts. For example, in the Sander Patent, U. S. 2,477,009 and 2,477,269, methods and apparatus are disclosed for coating a fluid upon particles of a moldable solid material by tumbling the material in dry particulate form while applying a spray of the fluid to the surface of the tumbling particles. In such processes it has been necessary to employ a fine mist of the lubricating fluid and this is a rather difficult and troublesome operation especially in those instances in which the liquid is to be applied is relatively non-volatile. Volatile lubricating oils can be applied in the form of a mist with less difficulty but, in general, solid particles coated with volatile lubricating oils have to be used promptly after application of the lubricant. A need has thus arisen for a simpler method for applying the lubricant, and also for a method which is less troublesome when used in the coating of polytetrafluoroethylene with relatively non-volatile lubricants.

The production of a homogeneous blend of polytetrafluoroethylene particles and lubricating oil by simple mixing of the ingredients in the proportions required in processes for production of shaped objects has not been feasible heretofore because, in view of the relatively small volume of oil employed per unit volume of powder, excessive mechanical treatment is required to assure the coating of each particle with the lubricating liquid. Temps have been made to produce the desired effect by admixing the powder polymer with an excess of the lubricating oil followed by squeezing out the excess through the use of a filter plate or porous piston. It has not been possible to achieve any practical success by employing the latter method, partly because of the difficulties associated with the use of porous diaphragms or plates and also because this method produces a non-uniform paste, having less lubricant at the surfaces of the filter cake than in the interior.

It has been discovered in accordance with this invention that polytetrafluoroethylene-lubricant pastes in which the lubricant is uniformly distributed throughout the entire mixture can be prepared by admixing particulate polytetrafluoroethylene with the quantity of lubricating oil hereinafter defined until a non-uniform mixture is produced and thereafter compressing the said mixture into a confining space until the lubricant, as a result of the said compression, becomes uniformly distributed throughout the mass.

In admixing the particles of polytetrafluoroethylene with the lubricant, it is essential to avoid excessive lumpiness and this can be achieved by rolling the polytetrafluoroethylene powdery mass after adding the lubricant thereto. It is also desirable, immediately after mixing the powder and lubricant, and before starting the rolling action, to shake the mass vigorously so as to break up any large lumps which may have formed during the addition of the lubricant to the polymer. This rolling action does not distribute the lubricant uniformly over the surfaces of the particles but it produces a non-uniform mixture of oil and powder which can be made uniform by compression. The effect of compression is to force the oily lubricant into the air spaces still remaining throughout the mass and thus produce a pasty mixture which can be shaped in any manner which may be desired, such as by extrusion or compression molding. The confining space which is essential in the compression step may be a pressure-resistant cylinder or any other shaping means into which the lubricant-polymer mixture can be forced under hydrostatic pressure.

The compressed polymer which is obtained as above described is of a dusty or putty-like consistency. It can be shaped and sintered to produce a much stronger article by methods hereinafter disclosed. The pressure required for converting the non-uniform lubricant-powder mass to the compressed paste-like mass, in which the lubricant is uniformly distributed, is generally at least about 50 lbs./sq.in. and is usually within the range of about 50 to 500 lbs./sq.in. or slightly higher.

The temperature employed in the mixing step and also in the compression step may be varied over a rather wide range but ordinary temperature, i.e. room temperature, is entirely suitable.

The quantity of lubricating oil employed is highly critical and is within the range of 7 to 45 cc. of oil per 100 grams of polymer. For optimum results, the quantity of oil must be precisely controlled; for example, when the lubricating oil is a mixture of 1 to 3 parts by weight of "Vistanex" polyisobutylene per 100 parts of hydrocarbon solvent which can be volatilized under the conditions hereinafter described, the critical quantity of lubricant is within the range of 27 to 35 cc. per 100 grams of polymer, for production of articles having optimum strength.

The lubricating oils which may be employed in the practice of the invention include any of the organic lubricants which can be removed from polytetrafluoroethylene by heating at temperatures below the decomposition temperature of the polymer. Solutions of polyisobutylene in volatile or relatively non-volatile organic solvents produce satisfactory results. Any hydrocarbon lubricant, especially those having a viscosity within the range of from 1 to 100 centipoises, may be employed. The recommended viscosity of the lubricant for practicing the invention in the best possible manner is about 3 to 5 centipoises.

While the invention is uniquely well adapted for the use of relatively non-volatile lubricants, which can be employed with difficulty in the previously known mixing processes, it is to be understood that the volatile lubricants or lubricants having volatile components may be employed equally satisfactorily, or even with preference, in the practice of this invention, especially in those appli-
cations in which the pasty composition is employed immediately after it is prepared.

In practicing the invention, polytetrafluoroethylene of any particle size may be employed. For best results it is important to employ a powder which can be passed through a 10 mesh screen. Powders in which the particles are of colloidal size may be employed very effectively but it is not necessary or essential that the particle size be of such small magnitude.

Any suitable method may be employed for mixing the lubricant with the polymer powder. Exceptionally excellent results are obtained by placing the polytetrafluoroethylene powder in a rotating vessel after screening it through a 10 mesh screen, forming a crator in the said powder in the container, and pouring the critical amount of lubricant into the crater thus produced. In this method of operation care should be taken that the lubricant does not come in contact with the container walls but that it remain as a pool in the center of the powdery mass, whereby it can seep through powder particles before reaching the walls of the container. If a lubricant containing a volatile component is employed, it is desirable to close the container promptly at this stage of the process to prevent excessive evaporation of the volatile lubricant component. If the lubricant has seeped into the polytetrafluoroethylene powder mass, i.e., when the pool of lubricant has been partially or substantially dissipated, the container may be shaken vigorously for a few minutes to break up any lumps which may be present. After this the container is placed in a rolling device, and the entire mixture is rolled to produce a mass which, as hereinabove indicated, does not have the lubricant uniformly distributed therein.

If desired, the non-uniform mixture of lubricant and powder can be compacted either by hand through the use of any of the known devices capable of exerting a compacting pressure. The product formed in this step, as described hereinabove, is thick and paste-like and can be smeared between the fingers into a film. This paste can be extruded in the form of tubes, rods, etc.

If a relatively volatile lubricant or lubricant component has been employed, the tube or other shaped article from the extruder should be heated at a temperature of about 100°C to 300°C to remove the said volatile component. It can also be removed by slow vaporization at room temperature, if desired. In any event, the mass should generally be heated, the temperature being ultimately raised to from 325°C to 390°C, to remove any lubricant, or lubricant thickener which may be present, and to sinter the polytetrafluoroethylene into a strong non-porous article. The time required for removal of lubricant depends upon the nature of the material to be removed. The heating should be so controlled that bubbling does not occur during the lubricant removal or sintering steps. The time required for removal of all traces of lubricant depends upon the size of the article which is being produced; for example, only a few minutes are required for removal of lubricant from thin walled small tubing, while for large tubing with thin walls one-half hour is generally sufficient, and up to one hour may be required for large tubing with heavier walls. The sintering should be performed with the tubing free to shrink. The causes of shrinkage are the coalescence which attends sintering, as well as the relaxation of stresses introduced by extrusion and the volume reduction attending lubricant removal. Up to 40% shrinkage generally occurs, most of this being in the machine direction. Sintered tubing prepared as described above is characterized by low permeability, chemical inertness, high dielectric strength, low power factor, and low dielectric constant. It is useful as flexible cable sheathing, and as slip-on insulation for hook-up wires. It is also readily adaptable for conversion to various shapes which can be produced from tubing by methods involving infra-red welding, cutting to form sheeting or tape, etc.

The polymer which is employed in the practice of the invention is polytetrafluoroethylene, and it is to be recognized that in certain instances homopolymers have end groups from molecular fragments which can be supplied by catalysts or other substances present during the polymerization of the polymerizable monomer, i.e., polytetrafluoroethylene. The polytetrafluoroethylene is preferably quite pure and water-free although non-essential ingredients such as small amounts (up to a few percent) of pigments which will withstand the sintering temperature may be present. Fillers including those which increase strength and rigidity as disclosed in Weidman application S. N. 306,301, may also be employed as desired but such fillers are, of course, not essential or necessary. A typical lubricant-polymer composition which can be employed in the manner hereinabove described is the following.

<table>
<thead>
<tr>
<th>Parts</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Teflon&quot; tetrafluoroethylene resin</td>
<td>81.0</td>
</tr>
<tr>
<td>V. M. P. naphtha (specific gravity .74 boiling range</td>
<td>90° to 170° C.)</td>
</tr>
<tr>
<td>1  *chrome yellow pigment</td>
<td>1.8</td>
</tr>
<tr>
<td>25  *Vistalex polyisobutylene thickener</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\* Medium Y-409-DR from the Pigments Division of E. I. du Pont de Nemours & Company, Inc.

The invention is illustrated further by means of the following example.

**Example**

200 g. of polytetrafluoroethylene powder was admixed with 40 g. (54 cc.) of white oil No. 30, thickened with 2% by weight of polyisobutylene, until a fluffy powder, comprising free-flowing particles admixed non-uniformly with oil, was obtained. This mixture was compressed in a 2 inch inside diameter die by applying a piston under 300 lbs./sq. in. pressure at room temperature for 15 seconds. A cylinder about 3 inches tall was thus produced, having density of about 1.5, and having excellent homogeneity in terms of lubricant concentration. The constancy of the lubricant concentration throughout the mass was determined by analyzing several slices weighing about 10 g. each, and the measurement of the oil content in these samples proved that no stratification of the lubricant concentration had occurred. Cylindrical cores thus produced were introduced into an extruder, and tubing was extruded therefrom heated at 150°C. This tubing was thereafter heated at 375°C. which produced a very strong thin-walled flexible tubular article having very low permeability and high dielectric strength.

Since numerous embodiments of the invention will occur to those skilled in the art, it is to be understood that the invention is not limited except as set forth in the following claims.

I claim:

1. The method for lubricating particulate polytetrafluoroethylene and improving the extrudability thereof which comprises admixing particles consisting essentially of polytetrafluoroethylene with from 5% to 45% of lubricating organic liquid per 100 grams of said polytetrafluoroethylene, said lubricating organic liquid consisting essentially of hydrocarbon oil, under a uniform free-flowing mass of powder and lubricant is formed, and thereafter compressing the said mass into a confining space under a pressure of at least 50 lbs./sq. in. until the said lubricant becomes uniformly distributed through the mass as a result of the said compression, whereby a pasty mass which can be readily extruded is obtained, said lubricating organic liquid having a viscosity within the range of from 1 to 100 centipoises.

2. Process of claim 1 wherein the said lubricant is a hydrocarbon oil having polyisobutylene dissolved therein as a thickener.
3. Process of claim 1 wherein the compacting pressure is within the range of 50 to 500 pounds per square inch.

4. The method for lubricating particulate polytetrafluoroethylene and improving the extrudability thereof which comprises admixing particles consisting essentially of polytetrafluoroethylene with a cc. of lubricating organic liquid until a non-uniform free-flowing mass of powder and lubricant is formed, said lubricant containing from 1 to 3% by weight of polyisobutylene thickener dissolved in a hydrocarbon solvent which can be volatilized at a temperature of 100 to 300° C., the quantity of said lubricant being from 25 to 35 cc. per 100 grams of the said polytetrafluoroethylene, and thereafter compressing the said mass into a confining space under a pressure of at least 50 lbs./sq. in. until the said lubricant becomes uniformly distributed throughout the mass as a result of the said compression whereby a pasty mass which can be readily extruded is obtained.

References Cited in the file of this patent

UNITED STATES PATENTS

2,440,190 Altham ---------------- Apr. 20, 1948
2,510,078 Compton et al. ----------- June 6, 1950
2,578,523 Llewellyn -------------- Dec. 11, 1951