United States Patent Office 2,881,142 Patented Apr. 7, 1959

2,881,142

POLYTETRAFLUOROETHYLENE AQUEOUS PASTE AND PROCESS FOR SHAPING SAME

John Emerson Eldridge, Newark, N.J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 8, 1954 Serial No. 454,845

3 Claims. (Cl. 260—17)

This invention relates to thickened aqueous pastes of polytetrafluoroethylene and to the manufacture of articles by processes which involve the extrusion or shaping of polytetrafluoroethylene in thickened aqueous paste form.

It has been known for some years that aqueous colloidal dispersions of polytetrafluoroethylene can be extruded into a coagulating medium to produce filaments, tapes, films, etc. which on subsequent sintering become quite strong (Barry U.S. 2,559,750, issued July 10, 1951). It has also been disclosed heretofore that polytetrafluoroethylene can be molded by cold-pressing finely divided polymer to the desired shape and thereafter sintering the shaped article (Brubaker et al. U.S. 2,400,099, issued May 14, 1946, and Benning et al. U.S. 2,400,094, issued May 14, 1946; cf. also the Fields Patent U.S. 2,456,262, issued December 14, 1948). More recently, it has been found that colloidal sized particles of polytetrafluoroethylene, coated with a hydrocarbon lubricant or other organic lubricant which is capable of being removed by the action of heat, can be extruded and the extrudate, after being freed of lubricant, can be sintered to form a tough product (Llewellyn and Lontz U. S. patent application S.N. 171,534, filed June 30, 1950, now U.S. Patent 2,685,707; Ind. Eng. Chem. 44, 1805–1810 (1952); 45, 1123–1127 (1953)). Quite generally, thickeners have been employed in hydrocarbon media in the latter process (Lontz application S.N. 171,533, filed June 30, 1950, now abandoned, and Lontz S.N. 389,160, filed October 29, 1953, now U.S. Patent 2,718,452) and such thickeners have been, in general, materials which could be removed readily by the action of heat prior to or during sintering.

Injection molding of polytetrafluoroethylene in a granular or micropulverized form at a temperature in the range of 300° to 400° C. under a pressure high enough to prevent melting of the polymer has been disclosed in the Hahn and Mallouk U.S. patent application S.N. 405,654, filed January 22, 1954, now U.S. Patent 2,770,842, the effect of pressure in restraining the melting of polytetrafluoroethylene being disclosed in the Tordella U.S. patent application S.N. 375,822, which was filed on August 21, 1953, now U.S. Patent 2,791,806.

Attempts have been made to employ aqueous lubricants in the injection molding of polytetrafluoroethylene in place of the hydrocarbon lubricants disclosed in the aforementioned U.S. patent applications S.N. 171,533 and S.N. 171,534, but it has been found that water as a lubricant is not as effective as the hydrocarbon lubricants (including thickened hydrocarbon lubricants) which had given satisfactory results. The products obtained heretofore through the use of water as a lubricant were not as strong as those which were obtained with the preferred

hydrocarbon lubricants. The hydrocarbon-lubricated compositions were, however, inflammable, and the volatile components which were released during the processing of the hydrocarbon-lubricated compositions were a source of safety hazard unless appropriate precautions were taken.

An object of this invention is to provide a process for preparing shaped articles from tetrafluoroethylene polymer pastes in which the lubricant is composed of water and added ingredients which permit the use of water in place of the previously used inflammable lubricants. Another object is to provide compositions suitable for use in making such shaped articles. A further object is to shape such compositions whereby shaped articles are formed without any hydrocarbon lubricant being required. A still further object is to extrude such compositions into filaments, tubes, coatings on wires, film and the like. Other objects of the invention will appear hereinafter.

The present invention is based in part upon the discovery that in the use of aqueous lubricants in colloidal polytetrafluoroethylene pastes, the wettability of the unsheared particles by the aqueous lubricant, and the viscosity of the lubricant, are dominant factors in obtaining good results. In contrast with hydrocarbons, water does not have the inherent property of wetting colloidal polytetrafluoroethylene particles when such particles have been subjected to shearing, as explained hereinafter. One of the significant features of the present invention, in one of its particular embodiments, is the use of additives which not only affect the viscosity of the aqueous lubricant but which also impart ability to wet the colloidal particles of polytetrafluoroethylene. The viscosity of the lubricant is an important factor, of course, and should be controlled by the methods disclosed herein.

The wetting of the surfaces of polytetrafluoroethylene particles depends not only on the nature of the liquid with which the surfaces are to be wet but also upon the character of the polytetrafluoroethylene particle itself. One of the characteristics of colloidal polytetrafluoroethylene particles is their tendency to be converted to a fibrous form when rubbed together. This change in the nature of the particles greatly affects extrudability as well as the wettability of the particles by aqueous lubricants. Particles which have undergone this change can still be wet by hydrocarbon lubricants, and can be shaped in the presence of the latter lubricants. To a slight extent, this change in the character of the particles takes place, in certain instances, upon merely subjecting the aqueous dispersion to vigorous agitation to produce a coagulation thereof (as disclosed in the Lontz Patent U.S. 2,593,583). For this reason, the removal of the particles from the polymerization mixture (produced by dispersion polymerization of tetrafluoroethylene), when these particles are to be used in the process of this invention, is preferably achieved without vigorous mechanical working. The shaping of articles from the water-wettable particles (which have not been mechanically worked) should be done under conditions which do not involve conversion of the particles to fibrous form in advance of actual shaping of the article. This does not preclude extruding the aqueous pastes herein disclosed, but it does seriously interfere with molding articles of extruded or otherwise worked polymer. Shaping methods which do not involve preliminarily converting polytetrafluoroethylene particles to a non-wettable form are, however, entirely suitable, using the aqueous thickened lubricants disclosed herein.

After the polymer has been shaped, in the manner just described, it is freed of water by drying at sufficiently high temperature to permit rapid removal of the water. It is thereafter heated to sintering temperature to produce a shaped article of excellent strength, while at the same time decomposing the thickener component of the lubricant.

The polymers employed in the practice of this invention include polytetrafluoroethylene and tetrafluoroethylene polymer with end groups supplied by chain transfer agents such as alkanols.

The additives which are present in the aqueous lubricants employed in the practice of this invention may include materials which have a thickening and wetting action when present in very small concentration. Water thickeners, which at small concentrations are relatively ineffective for producing the desired viscosity and the required wetting effect, may be employed in high concentration, but it is disadvantageous to employ such materials requiring high concentration, because they are rather difficult to remove from the final shaped article and may decrease the rate at which it dries. In this connection, it is to be noted that an excessively rapid rate of drying, i.e. an unduly high drying temperature, must be avoided, because of the tendency for such articles to form blisters when the rate of drying is excessive. It is preferred to employ as thickeners materials, such as methyl cellulose ether, which are highly effective at minimum concentrations, i.e. which have the desired effect upon wetting power and viscosity even when present to the extent of as little as 0.1% based on the weight of polytetrafluoroethylene. Such materials are relatively easily removed from the final sintered article by burning off (i.e. oxidizing with elemental oxygen) without leaving any appreciable quantity of char. In contrast with this, additives which must be present in relatively high concentrations (e.g. 10% of the quantity of polytetrafluoroethylene) to produce the desired effect on wetting power and viscosity are rather difficult to remove during sintering or in a subsequent heating step and produce articles which are black and contain relatively large amounts of char. In some instances, the desired wetting power and the desired viscosity can be achieved by combining an agent which has the required viscosity-imparting property with a material which has the desired wetting agent.

Suitable examples of additives which are effective include methyl cellulose ether, polyvinyl alcohol, sodium carboxy methyl cellulose, polyethylene oxide, polyvinyl pyrrolidone, styrene/maleic anhydride copolymer, vinyl acetate/maleic anhydride copolymer half calcium salt. In the case of methyl cellulose ether, the quantity of thickener which gave excellent results could be as little as 1% of the quantity of polytetrafluoroethylene; in fact, as little as 0.1% was found to give good products. A preferred range is about 0.1 to 2.0%. With methyl cellulose ether or polyvinyl alcohol, as well as with numerous other thickeners, it was not essential to employ a wetting agent. However, "Triton" X-100 (which is an alkyl aryl polyether alcohol non-ionic surface-active agent, more specifically a polyethylene glycol-p-octylphenol ether made by Rohm and Haas Company) could be used to improve wettability with either of these compounds or with other thickeners.

The paste which is employed in the practice of this invention can be prepared by concentrating an aqueous dispersion of colloidal polytetrafluoroethylene by any of various means which are well known in the art (cf. also Marks and Whipple patent application S.N. 348,116, filed April 10, 1953, now abandoned).

In one of the methods for practicing the invention, the thickener is added to the concentrated dispersion (together with the wetting agent if desired), and the resulting mixture is further concentrated by evaporation, or by coagulation followed by decantation of water. Evaporation is the preferred method for concentration at this stage because this minimizes any loss of agents which enhance the viscosity and wetting power of the liquid phase. The evaporation can be carried out simply by maintaining the thickened dispersions on trays at temperatures of from room temperature to 120° C. In one method of preparing the paste, the evaporation is continued until the resulting residue can be lifted from the tray by means of a spatula and broken into small chips. These chips thus produced are free flowing and show no tendency to compact into larger lumps.

Another method of drying found to be feasible is to feed the thickened dispersion into the nip of two steam heated rolls enclosed by an evacuated box. Doctor blades are used to scrape the dried polymer from the rolls. Where the product obtained is too sticky for convenient handling, ammonium nitrate or carbonate can be added to reduce the sticking.

Another method of drying which is suitable for larger scale operation is the use of a horizontal endless belt upon which a layer of dry residue can be formed, the residue being capable of cracking off the belt as the belt passes over the pulley. The pieces of residue thus formed are readily broken into free flowing chips.

The dry powder obtained as above described is mixed with water to produce an extrudable paste. If desired, the water can be added as a spray into the mixture which can simultaneously be tumbled in order to distribute the water as uniformly as possible. Alternatively, the water can be added in bulk and distributed throughout the mixture by tumbling. It was found to be helpful to allow the mixture to stand in a closed container overnight before extrusion, for in this way the water can penetrate more completely by diffusion and capillary action into the interior of the larger chips. The quantity of water which is present in the paste is preferably the minimum which is necessary to produce sufficient lubrication. This quantity of water can be as little as 5% and generally is not in excess of 40% based on the weight of polymer. The quantity of water used is determined to some extent by the complexity of the desired shaped article. When the quantity of aqueous lubricant is too small, the driving force required to extrude the composition is unduly great. Good all-around performance is obtained from compositions containing about 18% water based on the total weight of polymer and other ingredients of the paste.

Example 1.—To an aqueous colloidal dispersion obtained by polymerizing tetrafluoroethylene is added with thorough mixing 1% by weight of methyl cellulose ether, based on the weight of polytetrafluoroethylene polymer. The water content of the resulting composition is reduced by evaporation, using a shallow tray in an oven set at 120° C., the depth of the mixture in the tray being initially ⅜ inch. When a solid residue which can be lifted from the tray is obtained, this dry agglomerated colloidal residue is removed and placed in a suitable container wherein it is thoroughly admixed with 18% of water based on the weight of the polymer. The resulting paste was extruded readily through a die and the extrudate, which was in the form of a pipe liner, was sintered at 327° C. to give an outstandingly strong, although black, pipe liner suitable for use for its intended purpose.

In the process illustrated above, fillers, such as finely divided carbon, etc., may be present in the aqueous paste prior to the shaping thereof.

The method illustrated in the example was appraised, with results which were satisfactory from the standpoint of the formation of strong articles, using the thickeners listed in the following table. The table also records the behavior of the respective products on heating to above the sintering temperature. The water-soluble cellulose ethers were generally effective and constitute a preferred class of thickeners for use in the practice of the invention.

TABLE

Thickeners for water-lubricated polytetrafluoroethylene pastes

Commercial Name	Composition	Effect of Thickener as a Lubricant Aid	Behavior on Heating Final Article
"Methocel" 4,000	Cellulose methyl ether	Excellent	Chars.
"Elvanol" 72-51	Polyvinyl alcohol	Good	Do.
"Sodium CMC" 4-WM.	Sodium carboxymethyl cellulose.	do	Do.
	Vinyl acetate/maleic anhydride copolymer half calcium salt.	do	Do.

The thickened pastes hereinabove described are composed of a coagulum of colloidal particles, constituting a phase made up of contiguous particles, the lubricant being interspersed within said coagulum, i.e. adjoining the surfaces of the coagulum without preventing contact between particles. Water insoluble materials are not included in the term "thickener" as used herein, and, of course, coating compositions which do not contain water soluble thickeners, even though other resinous components are present (as in U.S. 2,668,157) are not within the scope of this invention.

The compositions described in the foregoing illustrations can be shaped by simple compression, upon application of pressures of 1000 to 2000 p.s.i., which on subsequent drying can be sintered to tough sheet stocks suitable for use in gaskets or electrical insulation such as slot liners. In addition, complex shapes such as flanged diaphragms can be compression-formed in molds having the desired contours by charging the lubricated powder or chips and applying pressures up to 2000 p.s.i., followed by drying and sintering. The pastes can be shaped in numerous other ways also, provided, as explained above, the formation of the fibrous form prior to shaping is avoided.

Pastes obtained as hereinabove described can be extruded satisfactorily to produce smooth, flexible extrudates. In general, the unsintered extrudates obtained from these pastes have somewhat less elongation but slightly higher tensile strengths than similar unsintered extrudates made from oil-lubricated pastes. There is very little difference in toughness between the two types of extrudates. At a water content of about 18%, the driving force necessary for extrusion is about the same as for the best oil-lubricated pastes; at water contents below 18%, the aqueous paste requires more driving force to extrude.

The extrudate must be dried carefully before sintering in order to avoid blistering.

After drying, the shaped articles are subjected to a sintering action at temperatures of at least 327° C. This results in the charring of the thickener since the thickener "burns off" during the sintering step. The black color produced by "burning off" is not detrimental in certain applications, such as in pipe liners, but it may be objectionable in certain other applications. To eliminate charring, the sintering can be conducted in a ventilated oven whereby the shaped articles lose most of their color when heated at sintering temperatures for prolonged periods of time, namely about 45 minutes to three hours (for approximately 0.060 inch thicknesses). This method is quite effective for decolorizing thin articles but it is generally not employed for decolorization of relatively thick walled articles.

Still another method for avoiding the formation of dark-colored products is to include a small quantity of ammonium nitrate in the paste prior to extrusion. When this is done, the sintering of the extrudate causes the salt to decompose and liberate oxygen which "burns out" the carbon residues quickly. A disadvantage of this method is that it results in the formation of products which are not as tough as those which are formed in the absence of soluble salts. Thus the method chosen for avoiding the discoloring produced by charring is determined by the nature of the product which is desired or the use to which it is to be put, and in fact, the need for avoiding formation of charred products also depends on the properties which are desired in the final product.

The aqueous pastes which are employed in the practice of this invention are composed of tetrafluoroethylene polymer particles of colloidal size admixed with the hereinabove described lubricant mixture having a viscosity of 10 to 10^6 poises, or more. A characteristic property of the lubricant mixture is its capacity to wet polytetrafluoroethylene. The lubricant mixture is composed of water, and at least one organic additive including a thickener. The wetting power of the lubricant is enhanced by at least one of the said additives. One of the significant properties of the composition just described is the extrudability thereof. These compositions can be shaped as hereinabove described or extruded in other forms such as in the form of filaments or beading.

The shaped articles obtained in the practice of this invention can be used for a variety of applications including many of those for which shaped polytetrafluoroethylene articles, made from oil-lubricated polytetrafluoroethylene compositions, can be used. Particular examples include liners for pipes or chemical equipment, tubular products, etc.

I claim:

1. A composition comprising a coagulum of tetrafluoroethylene polymer particles of colloidal size and from 5 to 40% by weight of said tetrafluoroethylene polymer of a lubricant having a capacity to wet polytetrafluoroethylene, said lubricant being composed of water and at least one organic additive including from 0.1 to 10% by weight of said tetrafluoroethylene polymer of a polymeric water-soluble organic thickener therefor, said lubricant being interspersed in said coagulum, said polymeric thickener being a member of the class consisting of methyl cellulose ether, polyvinyl alcohol, and sodium carboxymethyl cellulose.

2. A process for preparing shaped articles which comprises shaping at a temperature below the boiling point of water a paste having the composition set forth in claim 1, said paste being further characterized in that it is composed of a coagulum of unsheared colloidal particles of tetrafluoroethylene polymer and a lubricant having a viscosity of 10 to 10^6 poises, said lubricant having the capacity of wetting said tetrafluoroethylene polymer, said lubricant being composed of water and at least one organic additive including a dissolved polymeric water-soluble organic thickener therefor, wetting power of the said lubricant being enhanced by at least one of the said additives, the quantity of said lubricant being such that the lubricated mixture contains from 5 to 40 parts by weight of water per 100 parts of said tetrafluoroethylene polymer, said lubricant being interspersed in said coagulum, said polymeric thickener being a member of the class consisting of methyl cellulose ether, polyvinyl alcohol, and sodium carboxymethyl cellulose.

3. Process of claim 2 wherein the said thickener is methyl cellulose ether and the quantity thereof is from 0.1 to 2.0% of the weight of polytetrafluoroethylene.

References Cited in the file of this patent

UNITED STATES PATENTS

2,478,229	Berry	Aug. 9, 1949
2,681,324	Hochberg	June 15, 1954