

EXTRUSION OF POLYTETRAFLUORO-ETHYLENE

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No Drawing. Application July 1, 1954,
Serial No. 440,858

9 Claims. (Cl. 18—55)

This invention relates to the fabrication of polytetrafluoroethylene articles by extrusion, more particularly by so-called paste extrusion and to improved paste compositions for this purpose.

Polytetrafluoroethylene, better known by its trade-name "Teflon," as it will hereinafter be called, may be formed into shaped articles in various ways including extrusion of dry, finely divided Teflon, accompanied or followed by heating to a temperature at which it sinters to form a homogeneous body. This process is limited to heavy-wall sections. For the making of thin-wall sections, for example thin-wall tubing, a more recently developed process known as "paste extrusion" has been developed. The present invention relates to the latter.

Teflon is not subject to the processing or forming techniques used with most other plastics because it does not melt or flow and cannot be dissolved. In the paste extrusion technique it is admixed in a finely divided state with a volatile organic lubricant, preferably made into preforms, extruded, heated to volatilize the lubricant and then sintered by heating to the required temperature, thus producing the finished product.

More specifically, a Teflon composition for the extrusion of thin-wall tubing has been prepared as follows: A thickened volatile lubricant was made up by dissolving one part by weight of "Vistanex" (LM-MS grade, Enjay Company of New Jersey), a polyisobutylene, in 16 parts by weight of VMP grade naphtha. To 830 grams of Teflon (Du Pont's "TE-3086" grade, a fine powder) 170 grams of said lubricant were added and thoroughly admixed by tumbling for a few minutes in a partly filled closed container. This moistened powder was then made into preforms in a press at room temperature under a pressure of from 10–50 p. s. i. and the preforms inserted in a ram-type extruder having a mandrel in the die orifice so as to produce tubing. The tubing produced is moist, soft, very fragile to the touch and of a fibrous character and is finished in two steps. First it is heated at about 300° F. until the volatiles are driven off and then it is heated further to above the transition temperature, which is about 621° F. until the product is sintered and becomes a tough, homogeneous body.

Now in producing tubing and the like by this process various difficulties have been encountered. The length of tubing which it has been able to make without defects such as splits, cracks and a seriously rippled surface has been limited to what can be extruded from a single preform charged into the extruder. This is due to the fact that the fresh charge of a second preform, put in behind the already compacted remains of a preceding preform, does not bond or unite with it and when the material at the junction of two preforms reaches the orifice of the extruder defects of the aforementioned character develop, either at once or during the sintering step. The reasons for this failure of successive preforms to unite are not as yet understood but it is possible that squeezing out of lubricant is a factor. Consequently the defective sections of the final product must be cut out and only short lengths

of sound tubing are obtained. Another type of observed defects may be described as blisters, pits or depressions on the inner or outer surfaces or in the tube wall which appear to be caused by excessive concentration of lubricant in localized areas. It will be understood that the lubricant and the Teflon are immiscible, since Teflon is insoluble, and hence the lubricant can and apparently does accumulate in spots under the pressure of extrusion. When this lubricant, which occupies space, is evaporated, a void or depression results which renders the wall thickness non-uniform and creates local weak spots. This is highly undesirable considering that such tubing is used for conveying fuels, oils and corrosive chemicals under pressure and often at high temperatures.

The present invention resides in the unexpected discovery of how the foregoing difficulties of the paste extrusion process may be overcome, enabling the production of continuous lengths of extruded product from a succession of preforms without defects at the junction areas and without the blisters or pits due to local concentration of lubricant. This is accomplished by the addition to the lubricated Teflon composition above described of a certain proportion of very finely divided, lubricant absorbent, inert material to the mix with an attendant alteration of the proportion of lubricant to maintain the desired rate of extrusion. In particular it has been found that a relatively small quantity of carbon black has the property of overcoming the difficulties above explained, when used as hereinafter more particularly explained. Instead of carbon black other materials such as silica flour, diatomaceous earth and the like may be employed as an extrusion aid. While we do not wish to be bound to any theory of the mechanism involved, it would appear that the additive functions to bring about a better distribution of the lubricant in the composition, maintaining this distribution under the conditions of extrusion and preventing concentration of the lubricant at surfaces of the preform in the extruder or in droplets within the extruded mass.

For a better understanding of how the invention is carried out in practice, the following is a specific example which has produced excellent results. A composition for extrusion was prepared of the following ingredients:

	Gms.
Teflon-TE 3086_____	810.
Carbon black_____	0.81
Naphtha-Vistanex sol'n_____	190.

The Teflon was first screened to break up lumps, weighed out and put in a 5 gal. glass jar. The stated quantity of carbon black (Cabot's "Supercarbovar," a channel black of fluffy composition) was then added to the Teflon and the jar tumbled on rollers until the two were thoroughly admixed. The 16 to 1 naphtha-Vistanex solution, the same as described above, was then poured into a pocket in the powder and tumbling resumed for from one to three minutes. The wet mixture was then screened through 1/8" mesh screen to break up lumps, taking precautions to avoid loss of solvent by evaporation, and returned to the jar for tumbling for about 15 minutes. Preferably the mixture is then stored for at least 16 hours at room temperature before use. Preforms may then be made by pressing the mix in a cylinder or other cavity, of a shape suited to fit the chamber of the extruder, under a pressure of from 10 to 50 p. s. i. When these preforms were successively extruded into thin-wall tubing in a ram-type extruder they bonded to one another without any defects and tubing could be extruded in any lengths desired.

In the foregoing example, hydrophobic silica (a Du Pont product) has been substituted for the carbon black in the same quantity with substantially the same beneficial effects.

In the above example the carbon black is only 0.1% by weight of the Teflon which is no more than enough to give a grey cast to the mix and to the freshly extruded product, although after sintering the tubing is black. This is apparently due to the greater transparency of the sintered Teflon. Experiments with varying amounts of carbon black have shown that less than 0.1% shows improved results, improvement being noticeable with as little as 0.01% but 0.1% appears to be about the lowest quantity for satisfactory commercial results. The optimum quantity will lie somewhere between about 0.1% and 1% depending on variables such as type of carbon black used, there being no real lower limit, and larger quantities may be used up to about 5%. This is a practical upper limit, below which increasing the amount of carbon black does not appear to produce any deleterious effects. However, it has been found that for each 0.1% of carbon black added the quantity of lubricant should be increased by about 0.5% to maintain the extrudability of the composition. If this is not done, the rate of extrusion drops markedly and the pressures in the extruder build up. Adding lubricant to overcome this is feasible only to a point which corresponds to a carbon black content of about 5% (25% added lubricant) beyond which the preforms will not hold together and the extruded product becomes impossible to handle. Successful extrusion therefore depends on a nice balance of the ingredients according to the principles above set forth.

The type of carbon black to be used is preferably one which is very finely divided, such as channel black with a particle size in the range 140–220 Angstroms (14–22 millimicrons). Various brands of carbon black vary in absorptivity of the lubricant which may require some experimentation to determine the optimum lubricant content of the composition.

In the foregoing, the Teflon composition has been one without any permanent additions other than the carbon black or other finely divided, inert absorbent additive, the lubricant being evaporated. For some uses, however, it is desirable to incorporate inert fillers in extruded Teflon articles. It has further been discovered that compositions of Teflon powder and filler which are otherwise quite incapable of extrusion become so on the addition of carbon black within the percentage range explained above. For example, an attempt was made to extrude a lubricated admixture of Teflon powder (TE 3086) and aluminum oxide ("Aloxite" powder) in which the Aloxite was 35% of the dry material. The preforms were crumbly and the extruded product fell apart and separated from the lubricant. However, the following composition extruded satisfactorily:

Teflon—TE3086	-----grs--	25.
Aloxite	-----grs--	13.5
Carbon black (Supercarbovar)	-----grs--	1.25
Naphtha-Vistanex sol'n	-----cc--	13.9

The composition which could not be extruded was the same as the above but without the carbon black, which in quantity is 3.25% of the total weight of Teflon and Aloxite. This addition produced preforms having good cohesion and the extruded product was easily handled and of good quality. It is thus evident that another advantage of adding carbon black and other finely divided inert materials of the kind above mentioned to compositions for extrusion by the lubricated paste technique is that it makes possible the extrusion of admixtures of Teflon and inert fillers, especially compositions containing larger quantities of fillers which are otherwise unextrudable.

With respect to the use of preforms above referred to, it will be understood that they are a convenient way of charging the chamber of a ram-type extruder. Since the material is preliminarily compacted in making the preform, more material can be introduced than would be the case if it were in the form of a loose mixture.

However, the same problems will exist with respect to the bonding of successive charges whether or not the charge is preformed or preliminarily compacted since the remnants of a charge in the extruder have been subjected to the high pressure of extrusion.

It is to be understood that many details of the foregoing description are for purposes of illustration and that they are subject to variation. For example, the lubricants used are those presently believed to be most desirable but other volatile liquids and liquid solutions having a viscosity of 3 to 5 centipoises are known to be good lubricants for extruding Teflon. The invention, therefore, is not to be limited to such details but is to be construed in accordance with the claims.

What is claimed is:

1. The method of extruding articles from a paste comprising finely divided polytetrafluoroethylene and a volatile lubricant which comprises distributing throughout said paste from 0.01% to about 5% by weight of carbon black, based on the weight of the polytetrafluoroethylene, and thereafter extruding said paste through an orifice.

2. The method of extruding articles from a paste comprising finely divided polytetrafluoroethylene and a volatile lubricant, said articles being free from defects caused by localized concentrations of said lubricant, which comprises distributing throughout said paste from 0.01% to about 5% by weight of carbon black, based on the weight of the polytetrafluoroethylene, and thereafter extruding said paste through an orifice.

3. The method of extruding articles from a paste comprising finely divided dry polytetrafluoroethylene powder and a volatile lubricant, said articles being free from defects caused by localized concentrations of said lubricant, which comprises distributing throughout said paste by admixture with the said powder before addition of said lubricant from 0.01% to about 5% by weight of carbon black, based on the weight of the said powder, and thereafter extruding said paste through an orifice.

4. The method of continuously extruding articles from a succession of preforms fed to a ram-type extruder and formed from a paste comprising finely divided polytetrafluoroethylene and a volatile lubricant, said articles being free from defects in the areas formed from a mixture of materials from two adjacent preforms, which comprises distributing throughout said paste from 0.1% to 5% by weight of carbon black, based on the weight of the polytetrafluoroethylene, and thereafter making preforms from the paste, feeding them in succession to the said extruder, and extruding the articles.

5. The method of continuously extruding articles from a succession of preforms fed to a ram-type extruder and formed from a paste comprising finely divided dry polytetrafluoroethylene powder and a volatile lubricant, said articles being free from defects in the areas formed from a mixture of materials from two adjacent preforms, which comprises distributing throughout said paste by admixture with the said powder before addition of said lubricant from 0.1% to 5% by weight of carbon black, based on the weight of the polytetrafluoroethylene, and thereafter making preforms from the paste, feeding them in succession to the said extruder, and extruding the articles.

6. The method of continuously extruding articles from a succession of preforms fed to a ram-type extruder and formed from a paste comprising finely divided polytetrafluoroethylene and a volatile lubricant, said articles being free from defects in the areas formed from a mixture of materials from two adjacent preforms, which comprises distributing throughout said paste from 0.1% to 1% by weight of carbon black, based on the weight of the polytetrafluoroethylene, and thereafter making preforms from the paste, feeding them in succession to the said extruder, and extruding the articles.

7. The method of extruding an article from a paste made from finely divided dry polytetrafluoroethylene and

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a substantial quantity of finely divided dry inert filler and a volatile organic lubricant which comprises distributing throughout said paste by admixture with the said dry ingredients before addition of said lubricant from about 0.1% to about 5% by weight of carbon black, based on the weight of the dry ingredients, adding sufficient lubricant to form an extrudable paste, and extruding said paste through an orifice to form said article.

8. The method of extruding articles from a paste comprising finely divided polytetrafluoroethylene and a volatile liquid lubricant which comprises distributing throughout said paste from 0.01% to about 5% by weight of pulverulent inert lubricant-absorbent material having a particle size of an order no greater than the particle size of channel black, based on the weight of the polytetra-

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fluoroethylene, and thereafter extruding said paste through an orifice.

9. The method of extruding articles from a paste comprising finely divided polytetrafluoroethylene and a substantial quantity of finely divided inert filler and a volatile lubricant which comprises distributing throughout said paste from 0.1% to about 5% by weight of carbon black, based on the combined weight of the polytetrafluoroethylene and the filler, and thereafter extruding said paste through an orifice.

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