

United States Patent
Hopkin

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[54] **POLYTETRAFLUOROETHYLENE
FABRICATION WITH
HEXAFLUOROBENZENE**

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Related U.S. Application Data

[63] Continuation of Ser. No. 610,192, Jan. 18, 1967,
abandoned.

[52] **U.S. Cl.**.....264/127, 260/33.8 F

[51] **Int. Cl.**.....B29f 3/00, C08f 45/30

[58] **Field of Search**.....264/127; 260/33.8 F

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[57] **ABSTRACT**

Polytetrafluoroethylene (ptfe) is fabricated into shaped
products with the use of hexafluorobenzene as a plasticizer.
The ptfe may be particulate, and may be fabricated by ram ex-
trusion. From 8 to 16 percent by volume of the hex-
afluorobenzene is mixed with the ptfe and maintained in con-
tact with it for long enough to be absorbed onto and just into
the surface of the ptfe.

7 Claims, 33 Drawing Figures

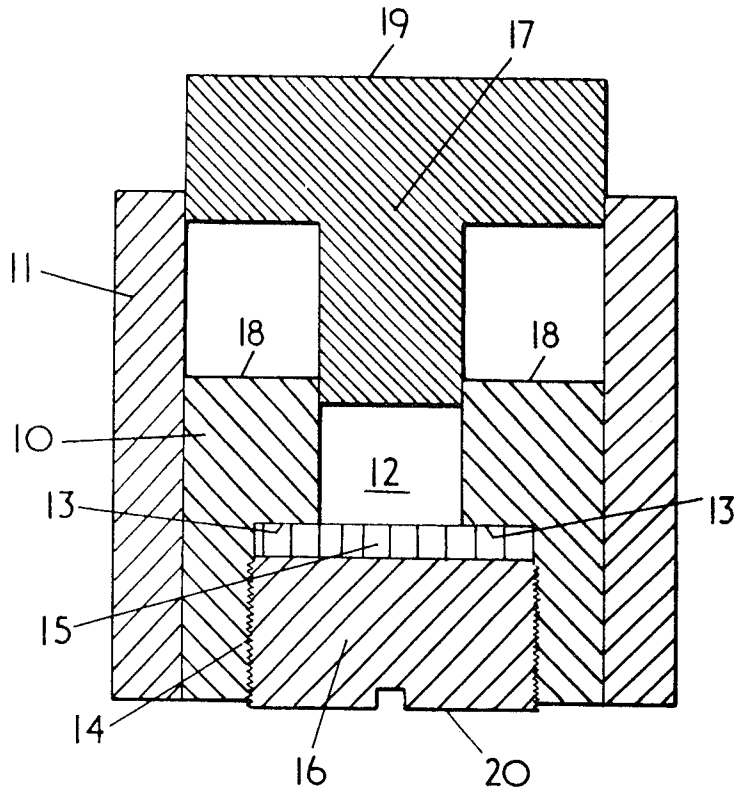
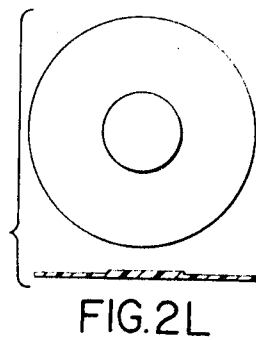
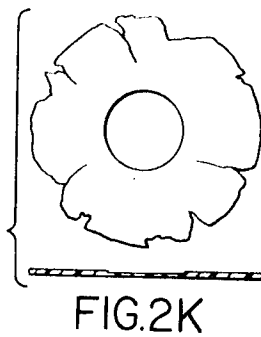
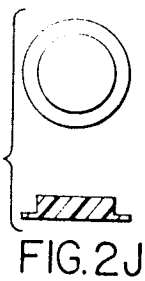
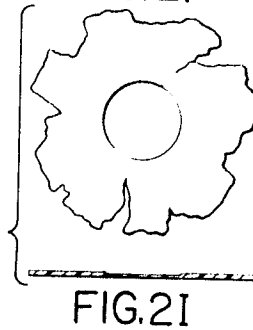
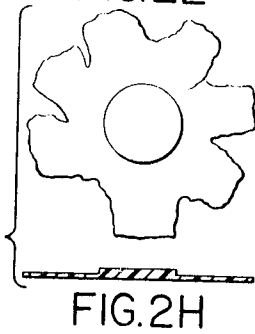
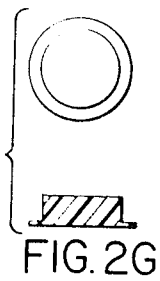
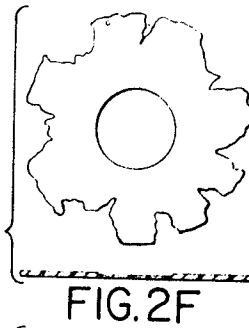
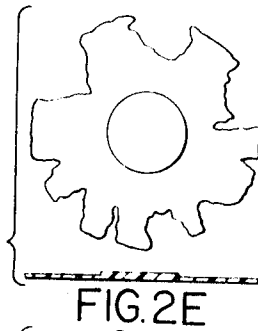
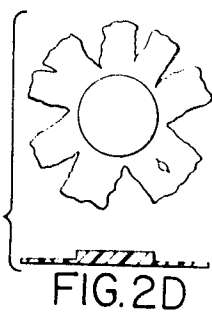
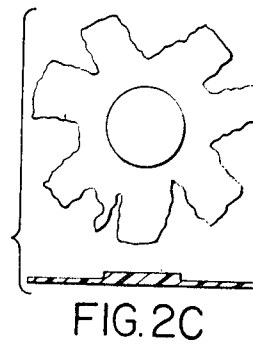
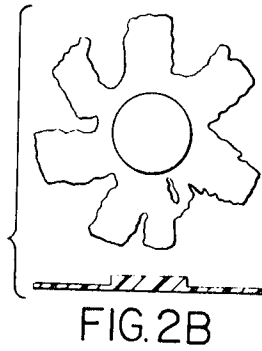
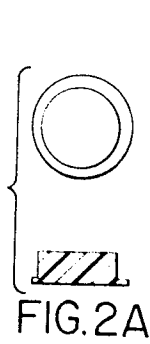


FIG. 1.

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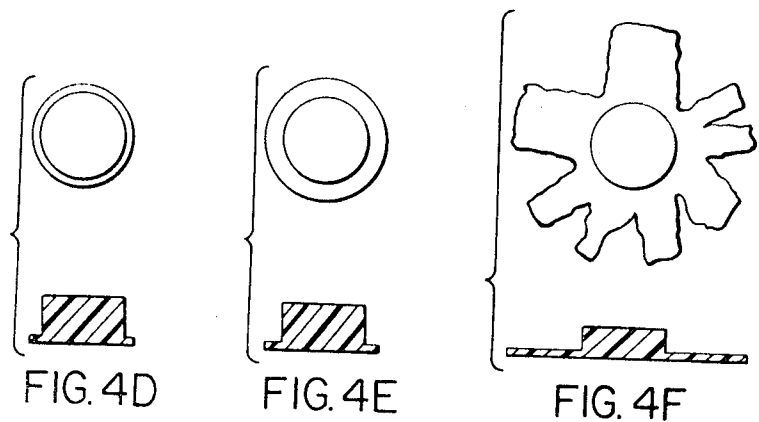
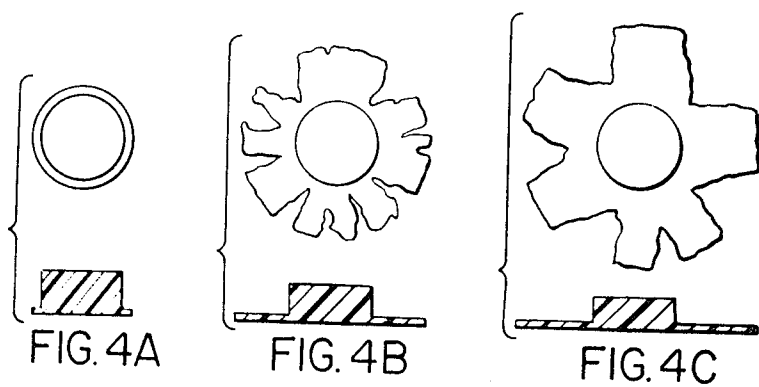
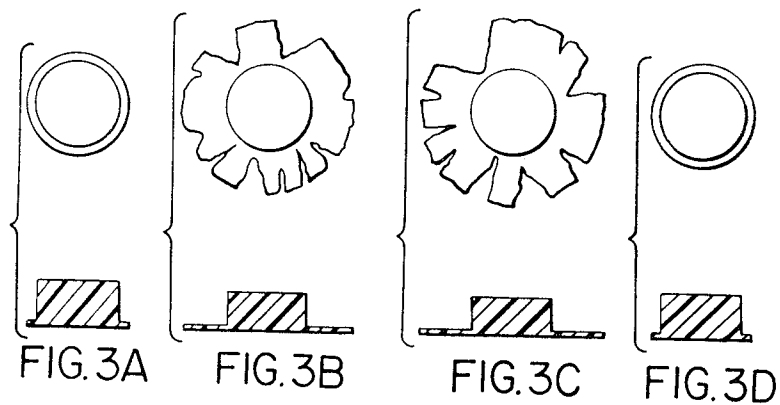
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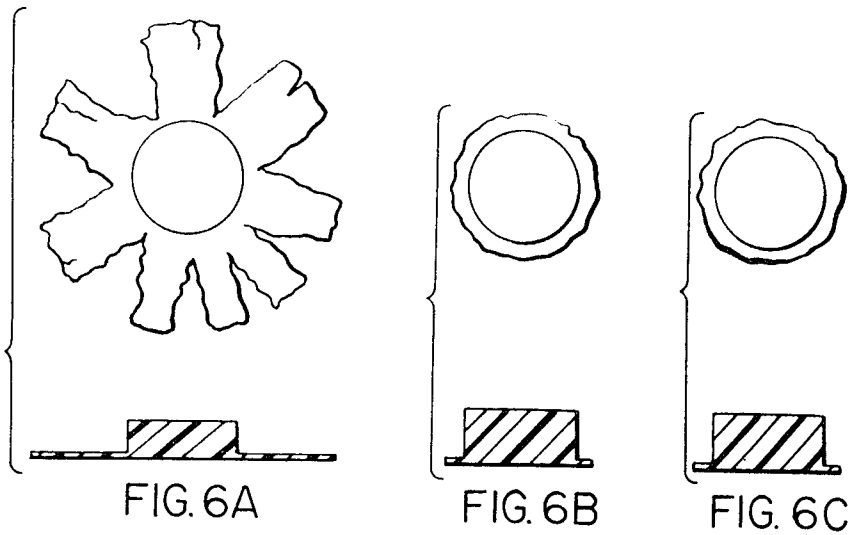
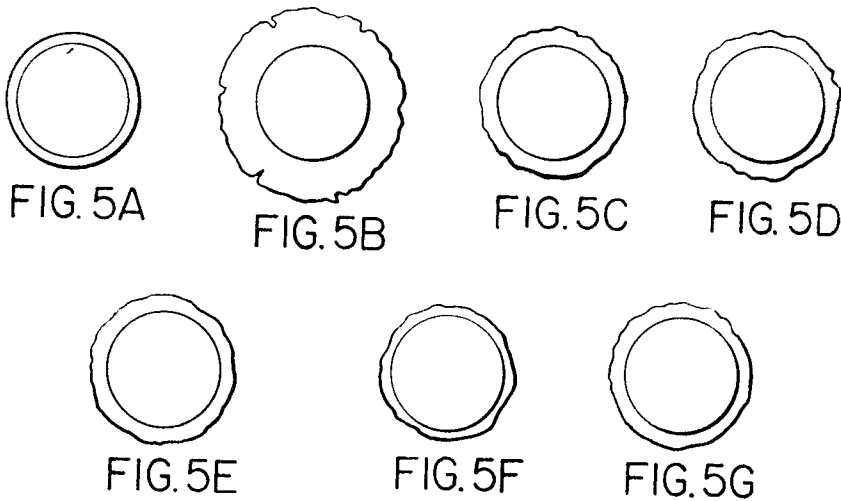
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POLYTETRAFLUOROETHYLENE FABRICATION WITH HEXAFLUOROBENZENE

This application is a continuation of application Ser. No. 610,192, filed Jan. 18, 1967 and now abandoned.

This invention relates to the fabrication of shaped articles from thermoplastic polymers.

In the fabrication of high melting thermoplastic polymers, it is frequently necessary to resort to the techniques of powder metallurgy in order to compact the moulding powder to a useful form. This is particularly necessary in the case of polytetrafluoroethylene. In this case, compacting by the use of high pressure in the cold compresses individual particles and closes up internal voids, and ensures large areas of contact between contiguous neighboring particles in the matrix. Subsequently, treatment at a temperature above the melting points of the crystallites, e.g. in the region of 380° C, enables a limited amount of flow to take place ("sintering") whereby the particles fuse together at the areas of contact.

However, two troublesome features of these operations are that complete expulsion of gases, and thus complete filling of the interstices of polymer during the cold compacting of granules is difficult, and voids are frequently observed after sintering; further high moulding pressures are required even to achieve these marginal improvements. Thus much effort has been expended in the development of polymer particles which minimise void formation.

The most frequent way in which this is carried out is by preparing polymer of finer particle size, but this makes the problem of flow of the raw polymer more and more difficult. The most satisfactory method for void-free polymer uses the so called paste extrusion process, but this is unsatisfactory as a process for producing shaped articles or mouldings. Further, this fine polymer is considerably more expensive than the granular grades.

The vital step in cold compacting is the compaction or the consolidation of the individual particles. If the particles, or even their surfaces were softer, more flow could take place, greater contact areas would result, and mouldings more free of voids and flaws would result. This condition is normally achieved by swelling the polymer with some volatile solvent. But cold compacting is also markedly improved if the polymer particles can be lubricated so that they "flow" under the pressure of the compacting device more easily and thus fill out the fixed dimensions of the compacting mould.

The present invention provides a method for the fabrication of polytetrafluoroethylene (referred to hereafter as ptfe) into a shaped product wherein it is processed in the presence of hexafluorobenzene.

The nature of such fabrication will generally be that granules or particles of ptfe are contacted with hexafluorobenzene in such quantity as to leave some hexafluorobenzene upon the surface of the granules or particles of ptfe, the particles or granules thereafter being subjected to some form of compaction, followed by heating to a sintering temperature.

The compaction is generally effected in a mould, but may also be carried out by ram extrusion, including thin-section extrusion. The presence of hexafluorobenzene with the ptfe greatly aids the extrusion of thin sections.

The present invention also provides a method of fabricating shaped products of ptfe, which method comprises mixing from 5 to 20 percent by volume, on the volume of the ptfe, of hexafluorobenzene with the ptfe, and then applying pressure to the ptfe to fabricate it into the desired shapes.

"Fabrication" in the preceding paragraphs includes compaction, prior to "sintering." It also includes welding of ptfe, in which process the surfaces to be welded are soaked or wetted with hexafluorobenzene, and are then welded by the application of heat and light pressure. Alternatively, a previously soaked thin strip may be interposed between the faces of a butt type weld. "Fabrication" also includes extrusion, whether ram extrusion or thin-section extrusion, for e.g. thin-wall tubing or wire sleeving. The invention is particularly advantageous when ram extrusion is performed, particularly when pressures below 5,000 psi are employed.

It is preferred to employ from 8 to 16 percent by volume, on the volume of the ptfe, of hexafluorobenzene. Proportions of hexafluorobenzene above 16 percent can be used, but the high cost of hexafluorobenzene tends to make the process less economical. For this reason, it is desirable to use the minimum, or at least a level approaching the minimum, effective amount of hexafluorobenzene. In ram extrusion equipment, or repetitive injection moulding equipment, a ram travels up and down as a piston, and batches of polymer granules are introduced from a hopper into the cylinder near the end of each cycle. Thus there is a measurable rate of flow of polymer through the machine, and thus a "residence time" of material in the hopper can be determined; clearly it will depend on whether batch-wise or continuous feed to the hopper is used. Thus, where continuous feed is in use, it is possible to mix the ptfe and hexafluorobenzene in the hopper, and, by careful control, maintain the residence time of the mixture in the hopper approximately constant.

For maximum economy of hexafluorobenzene the residence time under such flow conditions is important. We have surprisingly found that hexafluorobenzene is one of the very few organic solvents which will swell ptfe, either as a shaped sintered product or as raw polymer granules. But a period of time is needed to achieve equilibrium swelling of ptfe by hexafluorobenzene, which time period is determined by a variety of factors, the dimensions and surface area of the polymer particles being important ones. However, ptfe which has been allowed to swell to equilibrium with hexafluorobenzene, and which contains no excess hexafluorobenzene, shows no improvement in extrusion performance. Thus if it is desired to use less than the equilibrium amount, the residence time in constant flow equipment must be adjusted to be less than the time required to reach equilibrium swelling. Thus when 5 percent hexafluorobenzene, by volume on the volume of ptfe, is used a residence time of less than 1 hour, preferably in the region of 15 minutes will be necessary; where 10 percent of hexafluorobenzene, by volume on the volume of ptfe, is used a residence time of less than 6 hours, preferably in the range 1½ to 3 hours, is necessary. However, since no two machines perform the same, and no two samples of polymer have the same characteristics, the precise volume percentage required for a given residence time can only be determined by experiment.

In the case of batch-operated equipment the quantity of hexafluorobenzene, by volume on the volume of ptfe, will have to be a little higher than the equilibrium amount in order to overcome the lack of improvement found under conditions where all the hexafluorobenzene is absorbed into the body of polymer granules.

It will be appreciated that this process is applicable to the various grades of ptfe polymer available, that is to say, to the normal grade to fine grade and the ultra-fine grade. These particles or granules are more or less spherical or else are agglomerates of spheres.

Since the swollen and softened granules are fairly stable on storage, and may possibly in themselves figure as an article of commerce, it will be appreciated that granules or particles of ptfe mixed with hexafluorobenzene constitute another aspect of the present invention.

On sintering the hexafluorobenzene is volatilized and ptfe articles substantially identical with the conventionally prepared articles, with the exception of lower void content result, as may be shown by conventional physical testing and dye penetrant tests. (Thick section articles require special treatment in order to remove all the hexafluorobenzene; ageing at a more or less elevated temperature below the sintering point, e.g. about 300°C, with or without the use of a vacuum is effective.)

As indicated above, this process is not confined to moulding, since the essential feature of softening the surface of a polymer particle is capable of extension to all particle fabrication methods.

Thus, ram extrusion is made more effective. Ram extrusion takes polymer granules from a feed hopper which granules or particles are then compacted or consolidated by a ram.

Withdrawal of the ram allows more polymer granules to be charged on top of the largely consolidated billet for subsequent consolidation. The major weakness of this process lies in the absolute necessity for perfect welding of contiguous granule charges. Failure to ensure this results in transverse cracks and weaknesses. The use of hexafluorobenzene enables this welding of successive charges to take place much more readily, and substantially perfect billets are obtained with comparative ease. Further, thin-section extrusion e.g. of thin wall tubing or wire coatings, is also facilitated.

Compaction may be carried out substantially as normal, at temperatures from ambient to about 300°C. High temperatures can be disadvantageous in that premature volatilization of the hexafluorobenzene may result.

Recovery of the hexafluorobenzene is highly desirable because of its high cost; this may be carried out by conventional solvent recovery processes, e.g. pumping-off followed by refrigeration or absorption on charcoal and the like.

Conventional materials are also known which have the same effect of improving the quality of ptfе mouldings or extrusions. But these all suffer from the disadvantage that unlike hexafluorobenzene they are either not easily removable, or else not removable at all from the extruded matrix prior to sintering e.g. graphite and mineral oil. The presence of such materials in the extruded product renders the sintered product useless since they degrade under the sintering conditions.

The invention is further described with reference to the accompanying drawings, in which:

FIG. 1 is a sectional side elevation of an extrusion die, and

FIG. 2A-2L to 6A-6C each show ptfе samples (in plan and cross-section) extruded by the die.

Referring to FIG. 1, the die comprises a body 10 in a sleeve 11, the body having a cylindrical hole at 12 to contain ptfе granules, which hole is of enlarged diameter at its lower end below downwardly facing shoulders 13. The enlarged portion of the hole is screw threaded at 14. An aluminum disc 15, polished on its upper surface, bears against the shoulders 13, and is supported on a base plug 16 which is threaded at 14 and screws into the enlarged portion of the hole. A piston 17 fits into the sleeve 11 and the cylindrical hole at 12 with a clearance of from 0.003 to 0.005 inch. A 20TPI screw thread is used at 14.

In use, the threaded base plug 16 was screwed fully home against the aluminum disc 15, which in turn was pushed home

against the shoulders 13 of the body 10 of the die. The hole 12 was loosely packed with moulding material (approximately 11 gm of unadulterated ptfе filled the mould) up to the level of the top 18 of the body 10. The base plug 16 was unscrewed to leave a gap of 0.050 in. between the aluminum disc 15 and the shoulders 13; with the 20TPI thread used, this corresponds to backing off by one turn. The body 10 was then inserted into the sleeve 11, and the piston 17 put into place.

The assembled mould was placed in a hydraulic press, and the ram adjusted to zero pressure. The pressure was then built up across the faces 19 (top of the piston) and 20 (bottom of the base plug) uniformly to that desired (2,500, 5,000, or 7,500) over 1 minute, and maintained static at that pressure for 3 minutes. It was then released as quickly as the press allowed (less than 5 seconds). The die was then removed from the press, dismantled and the "top hat" removed (the extrusions are coherent enough to stand up to gentle handling).

Preparation of the moulding materials was effected as follows. The ptfе powder was rubbed through a 10 mesh sieve and the required amount weighed into a 4 oz. screw cap bottle, together with the required amount of additive. The bottle was then rotated at 200 r.p.m. approximately for the desired time. In control experiments the powder was merely rubbed through the sieve before use.

The loading of additive in all cases is based on the use of 1 volume of ptfе powder to x volumes of additive; thus a loading of 10 percent hexafluorobenzene is 10 ml. solid ptfе plus 1 ml of hexafluorobenzene. The weight of ptfе required is based on a solid density of 2.2 gm/cc.

FIGS. 2 to 5 shows the extrusions obtained from five series of experiments. In assessing the results, the two important parameters are

a. how much of the powder has been extruded from the body of the "hat" into the "brim" as indicated by the thickness of the remaining body

b. how far the powder has been extruded from the body of the "hat" into the "brim"

It should be borne in mind that these experiments were performed under very stringent conditions (0.050 in. is a narrow opening and 2,500 psi not a high pressure); the remark "unsatisfactory" indicates that good results would be obtained under these conditions of loading and contact time in commercial practice.

Figure	Additive	Proportion, ¹ percent	Mixing conditions	Pressure, p.s.i.	Remarks
2A	None			2,500	Bad.
B	do			5,000	Satisfactory.
C	do			7,500	Do.
D	Hexafluoro benzene	10		2,500	Do.
E	do	10		5,000	Do.
F	do	10		7,500	Do.
G	1,1,1-trichloroethylene	10		2,500	Bad.
H	do	10		5,000	Satisfactory.
I	do	10		7,500	Do.
J	Mineral oil	10		2,500	Poor.
K	do	10		5,000	Satisfactory.
L	do	10		7,500	Do.
3A	None			2,500	Bad.
B	Hexafluorobenzene	10	10 min. tumble	2,500	Satisfactory.
C	do	10	1.5 hr. tumble	2,500	Do.
D	do	10	20 hr. tumble	2,500	Bad.
4A	do	5	1.5 hr. tumble	2,500	Bad.
B	do	10	do	2,500	Satisfactory.
C	do	15	do	2,500	Do.
D	Hexafluorobenzene	5	20 hr. tumble	2,500	Bad.
E	do	10	do	2,500	Do.
F	do	15	do	2,500	Satisfactory.
5A	None			2,500	Bad.
B	Hexafluorobenzene	10	2 hr. tumble	2,500	Satisfactory.
C	1,1,1-trichloroethane	10	do	2,500	Bad.
D	Mineral oil	10	do	2,500	Do.
E	Molybdenum disulphide	10	do	2,500	Do.
F	Water	10	do	2,500	Do.
G	Graphite	10	do	2,500	Do.
6A	Hexafluorobenzene	10	10 min. tumble	2,500	Satisfactory.
B	do	10	10 min. tumble plus 24 hrs. standing	2,500	Bad.
C	do	10	24 hrs tumble	2,500	Do.

¹ By volume on volume of ptfе.

Determination of the Volume Equilibrium Swelling of Polytetrafluoroethylene by hexafluorobenzene.

This was carried out by two different methods on two separate samples of sintered ptfe sheet.

A. By observing the increase in volume of sample in contact with excess hexafluorobenzene.

Weights:	dry sample	0.8935 gm.
	swollen sample	0.9685 gm
Volume*:	dry sample	0.4194 cc.
	swollen sample	0.4641 cc.

*by displacement of water in a specific gravity bottle. Hence volume swell: 10.6%

B. By observing the length only of a strip immersed in excess hexafluorobenzene.

This method assumes that the product is anisotropic—which a sintered product rarely is; two strips were cut from the same sample.

Initial lengths:	7.215 cm,	7.148 cm
Swollen lengths:	7.375 cm,	7.323 cm
Equilibrium volume swellings:	6.80%, 7.52%.	

Thus in determining the minimum amount required, a volume measurement technique is required.

I claim:

1. A method for the fabrication of finely divided particulate polytetrafluoroethylene into a shaped product wherein 5 to 20 percent by volume of the polytetrafluoroethylene of hexafluorobenzene is mixed with the polytetrafluoroethylene par-

ticles, wherein said hexafluorobenzene is maintained in contact with said particles for such time as to ensure absorption of the hexafluorobenzene by the polytetrafluoroethylene to bring about swelling of the particles and to also ensure the presence of an excess lubricating amount of hexafluorobenzene, and applying pressure to the polytetrafluoroethylene particles to fabricate them in the desired shape.

2. A method as claimed in claim 1 wherein the hexafluorobenzene and the polytetrafluoroethylene are maintained in contact for a period of time not exceeding 1 hour when 5 percent of hexafluorobenzene is used and not exceeding 24 hours when 15 percent of hexafluorobenzene is used, the maximum contact time for intermediate proportions of hexafluorobenzene being intermediate the periods stated.

3. A method as claimed 1 wherein the range of hexafluorobenzene is from 8 to 16 percent by volume as compared to the volume of the polytetrafluoroethylene.

4. A method as claimed in claim 1 wherein the fabrication is performed by ram extrusion.

5. A method as claimed in claim 4 wherein the extrusion is performed at a pressure of not more than 5,000 psi.

6. A method as claimed in claim 5, wherein the extrusion is performed at a pressure of from 2,000 to 3,000 psi.

7. Finely divided granules or particles of polytetrafluoroethylene softened with and swollen by 5 to 20 percent volume of the polytetrafluoroethylene of hexafluorobenzene, said hexafluorobenzene being present in an amount in excess of that which is absorbed by said polytetrafluoroethylene in order to bring about said swelling.

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