PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{5} :
C08L 101/00, 23/02
// (C08L 101/00, 27/12)
(C08L 23/02, 27/12)

A1

(11) International Publication Number: **WO 91/05021**

(43) International Publication Date: 18 April 1991 (18.04.91)

(21) International Application Number: PCT/US90/05557

(22) International Filing Date: 4 October 1990 (04.10.90)

(30) Priority data:

418,376	6 October 1989 (06.10.89)	US
461,093	4 January 1990 (04.01.90)	US
572,921	29 August 1990 (29.08.90)	US
572,922	29 August 1990 (29.08.90)	US

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: CHAPMAN, George, Richard, Jr. ; 224 Wrights Lane, Media, PA 19063 (US). PRIESTER, Donnan, Edwin ; 215 Mullin Road, Wilmington, DE 19809 (US). STEWART, Charles, Winfield ; 4 Jobs Lane, Newark, DE 19711 (US). TARNEY, Robert, Edward ; 505 Summit Drive, Hockessin, DE 19707 (US).

(74) Agents: ROMBACH, Louis, H. et al.; E.I. du Pont de Nemours and Company, Legal Department, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States: AT (European patent), BE (European patent), BR, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESSING AID FOR POLYMERS

(57) Abstract

I. Polymer blend composition having improved processibility and comprising: 1) a difficultly-melt-processible polymer and 0.002 - 0.5 wt. % of one more fluoropolymer process aids wherein the fluoropolymer has a fluorine to carbon ratio of at least 1:2, is capable of forming a die-coating film under the prevailing conditions of extrusion temperature and pressure, and contains an effective amount of polar functional polymer chain end groups, -W, wherein -W is selected from -COF, -SO_3M, -OSO_3M and -COOM, wherein M is hydrogen, a metal cation, preferably an alkali or alkaline earth metal cation, or a quaternary ammonium cation; or 2) (a) a major portion of a difficultly melt-processible polymer and (b) a minor portion of: (1) at least an effective amount, to improve processibility, of a fluorocarbon copolymer which at the melt-processing temperature of (a) is either in a melted form if crystalline, or is above its glass transition temperature if amorphous, and (2) at least an effective amount, to improve processibility, of at least one tetrafluoroethylene homopolymer or copolymer of tetrafluoroethylene and at least one monomer copolymerizable therewith, wherein the mole ratio of fluorine to hydrogen is at least 1:1, and which is solid at the melt-processing temperature of (a); II. masterbatches comprised of a processing aid; and III. processes utilizing a processing aid.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Fasso
BG	Bulgaria
BJ	Benin
BR	Brazil
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CM	Cameroon
DE	Germany, Federal Republic of
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GR	Greece
HU	Hungary
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
RO	Romania
SD	Sudan
SE	Sweden
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
US	United States of America

TITLE

Processing Aid For Polymers

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a processing aid for polymers, and to polymers having improved processibility, particularly improved extrusion characteristics.

Background

The melt extrusion of high molecular weight polymers, for example, hydrocarbon polymers, into shaped structures such as tubing, pipe, wire coating or film is accomplished by well-known procedures wherein a rotating screw pushes a heated, molten and viscous polymer melt through the extruder barrel into a die in which the polymer is shaped to the desired form and is then subsequently cooled and resolidified, by various means, into the general shape of the die.

In order to achieve low production costs it is desirable to extrude at high rates. Although the extrusion rate is readily increased by increasing the rate of revolution of the extruder screw, there is a technical limit to these increases because of the viscoelastic properties of the polymer. At rates above this limit the polymer may be mechanically heated to temperatures at which thermal decomposition can occur, or extrudates with a rough surface are obtained. The latter phenomenon can generate an undesirable pattern on the surface of the extrudate. One way of avoiding this occurrence is to extrude at a higher temperature, but this adds to the processing costs and makes cooling of the extrudate more difficult. More seriously, many polymer resins are already extruded at temperatures near their decomposition temperatures, and further increases are not feasible.

Still further in this regard, in the melt extrusion of polymer resins there are often flow regimes, determined by the rheological properties of the particular resin, where anomalous flow behavior occurs leading to surface imperfections on the extrudate surfaces. Such imperfections, commonly called melt fracture, appear in different forms. The so-called "sharkskin" fracture occurs at lower shear rates and appears as a general, finely-structured and uniform roughness. In a blown-film extrusion sharkskin fracture may appear as an undesirable herringbone pattern, reducing clarity and giving a dull surface. In practice this may occur at uneconomically low extrusion rates. At higher shear rates flow often becomes unstable and a non-uniform stick-slip melt fracture results, wherein alternating bands of glossy surface and sharkskin fracture appear. This behavior is especially undesirable in wire coating and in tube and pipe extrusions as well as in blown-film applications.

Additional examples of poor extrusion behavior include formation of deposits of the extruding polymer resin, degraded polymer resin or resin additives around the die exit (orifice); surging in polymer flow and erratic pressure fluctuations that occur due to uneven pumping of the polymer melt, which may result in erratic fluctuations of output rate; and torquing out of the extruder, that is, overloading the pressure limit of the extruder, resulting in automatic shutdown of the extruder.

It is desirable, therefore, to find highly efficient means of increasing the extrusion rate, without raising the melt temperature, while producing products with smooth surfaces. Changes in extruder and die configuration can improve melt flow but are not always practical or economically feasible. Another approach involves the addition of conventional wax-type process aids which reduce bulk viscosity and in some cases improve processing properties. However, the efficiency is marginal and the high levels of additive required often adversely affect other properties.

In an effort to improve the extrusion behavior of polymer resins through metal dies it is known to coat the die surfaces that contact the flowing polymer melt with a slip agent, such as tetrafluoroethylene polymers and copolymers, as in Japanese Application Publication Kokai 55-82784 (Mitsui Petrochem. Ind., KK), but bonding to the metal is poor, and over a period of time in use the slip layer is depleted and melt fracture resumes.

In other practices, as for example in the extrusion of certain hydrocarbon polymers and copolymers, it is known to employ small amounts of fluorocarbon polymers, blended with the extrusion resin, as a continuously replenishing slip agent. Thus Blatz, in U.S. 3,125,547, discloses hydrocarbon polymer compositions having improved extrusion behavior that contain small amounts of fluorocarbon polymers that are above their glass transition temperature, if amorphous, or above their crystalline melting point (e.g. molten), if crystalline, at the process temperatures. Under these conditions the flow rate above which melt fracture occurs is greatly increased, and required extrusion pressures for a given extrusion rate are diminished. It is further taught in U.S. 3,125,547 that fluororesins which are solids at process temperature afford little or no improvements in extrusion characteristics of hydrocarbon polymers. By the term solid, it is meant that the fluororesin, if crystalline in nature, is not melted, or, if amorphous in nature, is not above the glass transition temperature.

Japanese Unexamined Application Kokai 1,074,247 describes the use of certain combinations of fluoropolymer process aids disclosed in U.S. 3,125,547, cited above. U.S. Patent 4,904,735 discloses the use of combinations of fluoropolymers that are molten at process temperatures, such as fluoroelastomers, and those that are not molten at process temperatures, such as crystalline tetrafluoroethylene homopolymers and copolymers.

Japanese Examined Applications Kokoku 55543/1988 and 55544/1988 describe compositions comprising a thermoplastic resin and a fluoropolymer process aid having pendant $-SO_3M$ groups, where M is an alkali metal anion.

Kamiya and Inui, in Japanese Patent Application Publication Kokoku 70-30574 (1970, examined) cite the use of crystalline fluorocarbon polymers at temperatures below their melting points to eliminate die build-up but say nothing of other extrusion improvements. Nishida, Tate and Kitani, in Japanese Patent Application Publication Kokai 62-64847, disclose injection molding compositions comprising an ethylene/alpha olefin copolymer having an MFR of 0.2-200 g/10 min., a density of 0.850-0.945 g/cm^3, and a Q value of 2.5-12, and 0.001-1% by weight of a fluorinated hydrocarbon polymer having an F/C ratio of at least 1:2.

Chu, in U.S. 4,740,341, discloses blends having improved extrudability and comprising a linear polymer of ethylene having incorporated therein

0.01-0.5 wt. %, based on the composition, of a fluorocarbon polymer having an F/C ratio of at least 1:2 and which is fluid at 120-300°C, and 0.01-0.5 wt. %, based on the composition, of a polysiloxane.

Larsen, in U.S. 3,334,157, discloses polyethylene which has been modified to improve its optical properties by incorporating therein 0.015 to greater than 1.7 % by wt., based on the mixture, of finely divided polytetrafluoroethylene.

It is an object of this invention to describe fluoropolymer compositions having effective concentrations of polar functionality and enhanced utility as process aids for the extrusion of difficultly-melt-processible polymers. The important effect of polar functionality situated on the fluoropolymer chain has not been heretofore recognized.

It is a further object of this invention to provide resin compositions with substantially improved extrusion characteristics. Another object is to provide polymers which can be extruded at high rates to give extrudates of high surface quality. It is yet another object to provide polymers that can be extruded at low die pressures and at low melt temperatures. Another object is to provide a processing aid by means of which all the above can be achieved. A further object is to provide masterbatches of the processing aid. Other objects will become apparent hereinafter.

SUMMARY OF THE INVENTION

First Major Embodiment of the Invention

One embodiment of the invention herein provides a composition having excellent extrusion characteristics. The composition comprises a difficultly-melt-processible polymer and

0.002-0.5 wt. %, preferably 0.01-0.2 wt. %, of one or more fluoropolymer process aids wherein the fluoropolymer:

(a) has a fluorine to carbon ratio of at least 1:1.5,

(b) has polymer chain ends bearing a functional group, W, wherein W is selected from $-COF$, $-SO_3M$, $-OSO_3M$ and $-COOM$, wherein M is hydrogen, a metal cation or a quaternary ammonium cation,

(c) is selected from the group consisting of

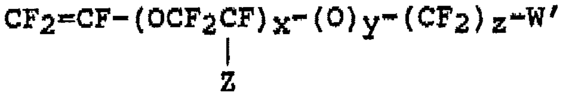
  (i) an irradiated polytetrafluoroethylene,

  (ii) a partially crystalline copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether) or a perfluoroolefin containing 3-8 carbon atoms,

  (iii) an elastomeric copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether),

  (iv) a copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, and

  (v) a copolymer of tetrafluoroethylene and 0.5-40 mole % of a functional-group-containing monomer



$$CF_2{=}CF{-}(OCF_2\underset{\displaystyle Z}{\underset{|}{C}}F)_x{-}(O)_y{-}(CF_2)_z{-}W'$$

  wherein Z is $-F$ or $-CF_3$, x is 0 or an integer of 1-4, y is 0 or 1, z is an integer of 1-12, and W' is selected from $-SO_2F$, $-SO_2Cl$, $-SO_3H$, $-COOR$ and $-COOM$, wherein R is C_{1-3} alkyl and M is hydrogen, a metal cation, or a quaternary ammonium cation, and

(d) contains at least 100 functional groups W per million carbon atoms.

The end-group functionality, W', can be introduced into the fluoropolymer process aid, for example: (1) as polymer chain end groups during polymerization, or (2) by subjecting polymer without the end groups to ionizing radiation.

Second Major Embodiment of the Invention

In another embodiment of the invention the processing aid consists essentially of, with the parts totaling 100:

(a) 2-95 parts by weight of a fluorocarbon copolymer which at the melt-processing temperature of the difficultly melt-processible polymer is either in a melted form if crystalline or is above its glass transition temperature if amorphous; and

(b) 98-5 parts by weight of a tetrafluoroethylene homopolymer or copolymer of tetrafluoroethylene and a monomer which is copolymerizable therewith, wherein the mole ratio of fluorine to hydrogen is at least 1:1, and which is solid at the melt-processing temperature of the difficultly melt-processible polymer.

This second major embodiment of the invention also consists of a polymer blend composition having improved processibility and which comprises:

(a) a major portion of a difficultly melt-processible polymer, the host polymer, and

(b) a minor portion of:

 (1) at least an effective amount to improve processibility, preferably to about 0.5 wt. %, based on the

weight of (a), more preferably 0.002 - 0.20 wt. %, of a fluorocarbon copolymer wherein, preferably, the mole ratio of fluorine to hydrogen is at least 1:1.5, which at the melt-processing temperature of (a) is either in a melted form if crystalline, or is above its glass transition temperature if amorphous, and

(2) at least an effective amount to improve processibility, preferably 0.002 - 0.20 wt. %, based on the weight of (a), of at least one tetrafluoroethylene homopolymer or copolymer of tetrafluoroethylene and at least one monomer copolymerizable therewith, wherein the mole ratio of fluorine to hydrogen is at least 1:1, and which is solid at the melt-processing temperature of (a).

For example, when the host polymer (a) is a hydrocarbon polymer, its melt-processing temperature generally will be in the range 100-250°C.

In summary, both major embodiments of the invention provide masterbatches containing the aforesaid processing aid; processes for facilitating the processing of difficultly melt-processible polymers; and difficultly melt-processible polymers containing the processing aid. A masterbatch, as the term is used herein, is a concentrate of the processing aid in a host polymer and consists essentially of a minor portion of the processing aid and a major portion of a polymer, either a melt-processible or difficultly melt-processible polymer, or both, for example, a hydrocarbon polymer.

BRIEF DESCRIPTION OF THE FIGURES

The figures which are a part of this specification are plots of die pressure (MPa) vs throughput (g/minute), showing the superior results achieved by means of this invention, as compared to those achieved by means of the prior art.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to fluoropolymers having utility in improving the extrusion behavior of difficultly-melt-processible polymer resins.

The invention is also applicable to difficultly-melt-processible polymers containing additives, for example, pigments and antiblock agents, such as silica, clays and glass beads. Light stabilizers, antioxidants and other common additives may also be incorporated therein.

The term "extrusion behavior" is intended to include, individually or in combination, such parameters as the operating melt temperatures, die pressure reached during extrusion, maintenance of a steady die pressure during extrusion, maximum extrusion rates that can be achieved, maintenance of a steady extrusion rate, dimensional stability of the melt, absence of deposits of decomposed polymer or additives at the exit of the die surface and good surface quality of the extruded part. In some cases the invention may provide a means for carrying out the extrusion at a lower temperature. Blow molding, tubing manufacture and fiber spinning represent examples of extrusion processes that may be improved by means of this invention. Thus, the compositions of this invention, compared to polymers not containing the processing aid of the invention, will show improved extrusion behavior, incorporating improvements in at least some of the parameters noted above.

Difficultly-melt-processible polymers are defined as those that either require uneconomically high extrusion pressures or temperatures for extrusion or extrude with unacceptable melt fracture, such that the surfaces of the extrudate are blemished under conditions that would be otherwise technically feasible or economically attractive; those that give excessive deposits of resin, decomposed resin or additives at the die exit (orifice); those that extrude under conditions such that large fluctuations in barrel or die pressure are experienced, sometimes to the extent that the pressure limit of the extruder is reached, resulting in automatic shutdown of the extruder.

Examples of difficultly-melt-processible polymers that may be operable in connection with the compositions and processes of the invention include the following: mono-olefin polymers, such as ethylene homopolymers and copolymers; vinyl aromatic polymers, such as polystyrene; copolymers of alpha-olefins, particularly ethylene, with vinyl esters, such as vinyl acetate and vinyl propionate, with (meth)acrylic esters, such as ethyl or methyl (meth)acrylate, with acrylonitrile, and with (meth)acrylic acids and their (ionomeric) metal salts and the like; chlorinated polyethylene; polyvinyl chloride; polyester; and polyamide. The difficultly-melt-processible polymer may also be a polymer blend or polymer alloy. As used herein, the term "alloy" is intended to describe compositions obtained by melt compounding of polymeric components containing co-reactive functional groups. As an example of such an alloy is an alloy comprised of a polyamide 6/6, an ethylene/n-butyl acrylate/methacrylic acid copolymer and an ethylene/n-butyl acrylate/glycidyl methacrylate copolymer.

In the case of a hydrocarbon polymer component of a composition of this invention, it may comprise an elastomeric copolymer of ethylene and propylene and, optionally, a non-conjugated diene monomer, for example, 1,4-hexadiene, or, in general, any thermoplastic hydrocarbon polymer obtained by the homopolymerization or copolymerization of a monoolefin(s) of the formula $CH_2=CHR$, where R is H or an alkyl radical, usually of not more than eight carbon atoms. In particular, this invention is applicable to polyethylene, both of the high density type and the low density type, for example, densities within the range 0.89 to 0.97; polypropylene; polybutene-1; poly(3-methylbutene); poly(methylpentene); and linear low density copolymers of ethylene and an alpha-olefin such as propylene, butene-1, octene-1, hexene-1, decene-1, octadecene, or 4-methylpentene-1.

When the difficultly-melt-processible polymer is a hydrocarbon polymer that is used, for example, in blown film extrusion, it will generally have a melt index (ASTM D-1238) at 190°C of 5 or less, preferably 3 or less. For a high shear operation, such as fiber extrusion or injection molding, even higher melt index resins, for example, having a melt index of 20 or more, may suffer extrusion difficulties.

Difficultly-melt-processible polyesters include condensation polymers derived from dicarboxylic acids and dialcohols and/or from hydrocarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polybutylene terephthalate and poly-1,4-dimethylolcyclohexane terephthalate.

Difficultly-melt-processible polyamides and copolyamides are derived from diamines and dicarboxylic acids and/or amino acids or the corresponding lactams, such as polyamide 6, polyamide 6/6, polyamide 6/10, polyamide 11 and polyamide 12.

It will be recognized by those skilled in the art that for those resins that extrude at high temperatures and, in addition, are chemically sensitive, for example polyester or polyamide, it is important to select fluorocarbon process aids that are thermally and chemically stable at the process temperatures. Generally speaking, such polymers are those that are very nearly perfluorinated, such as homopolymers of tetrafluoroethylene or copolymers of tetrafluoroethylene and other perfluoroolefins. Polyvinylidene fluoride and copolymers of vinylidene fluoride and hexafluoropropylene, for example, may dehydrohalogenate at temperatures in excess of about 250°C and are of lesser utility under these conditions.

Because of the different extrusion characteristics of the various polymers operable herein, the utility of the process aid of this invention may be of greater value with some polymers than with others. Thus, for example, hydrocarbon polymers, such as polypropylene or branched polyethylene, that are not of high molecular weight, have good melt flow characteristics even at low temperatures, so that surface roughness and other surface defects can be avoided by adjustment of extrusion conditions. Such hydrocarbon polymers may not require the use of the process aid of this invention, or be noticeably improved by it, except under unusual, adverse extrusion conditions. However, other polymers, such as high molecular weight, high density polyethylene or linear low density polyethylene copolymers, and high molecular weight, polypropylene and propylene/alpha-olefin copolymers, particularly those with narrow molecular weight distributions, do not have this degree of freedom in the variation of extrusion conditions and it is particularly with these resins that remarkable reductions in extrusion pressure and/or improvements in the surface quality of the extruded product are obtained by the compositions and processes of the invention.

It will be recognized by one skilled in the art that it may not be possible to achieve, simultaneously, reduced die pressure, increased throughput, improved surface quality and reduced pressure fluctuations to the maximum extent at a given concentration of fluoropolymer process aid. Thus, one might elect to attain maximum improvement in one parameter at the expense of corresponding improvements in other parameters. For example, increased output of extrudate with high quality surface characteristics may not necessarily be accompanied by reduced die pressure. Similarly, in some systems substantial reductions in operating die pressures are achieved, but without significant improvements in extrudate surface qualities. Reductions in pressure fluctuations or elimination of die buildup may be achieved, but without further improvements in surface quality. Alternatively, and for matters of operating economies, it may be desirable to operate at very low levels of fluoropolymer process aid rather than to achieve the maximum improvements in extrusion parameters achievable at higher concentrations. The best set of conditions will be determined by the specific requirements of the extrusion.

The addition of the fluorocarbon polymer process aid to the difficultly-melt-processible polymer can be accomplished by any of the means heretofore developed for the addition of modifiers to such polymers. The fluorocarbon polymer may be added, for example, to a hydrocarbon polymer on a rubber compounding mill or in a Banbury or other internal mixer or in a mixing extruder. When the fluoropolymer process aid is a non-massing powder, it is also feasible to dry-blend the fluoropolymer process aid with the host polymer in the solid state, and then effect uniform distribution of the fluoropolymer in the melt extruder employed in the fabrication by using an extruder screw with good mixing capability.

Alternatively, in some cases, masterbatch dispersions of the fluoropolymer process aid in a diluent polymer can be metered to the feed section of the extruder by appropriate devices or dry-blended with the host polymer prior to extrusion. Exceptions to this practice may apply with fluoropolymer process aids that are not necessarily melted at extrusion process temperatures. When such process aids are heated to higher temperatures in the masterbatch-forming process, under which conditions fluoropolymer particles may coalesce to larger particles, they are not appropriately subdivided in the final extrusion of the difficultly-melt-processible polymer. The diluent polymer can be a difficultly-melt-processible polymer, or it can be a melt-processible polymer that does not substantially deleteriously affect the interaction of the aforesaid fluoropolymer process aid with the metal surfaces of the extrusion die. For example, when the difficultly-melt-processible polymer is linear low-density polyethylene, the diluent polymer can be a melt-processible hydrocarbon polymer, such as a homopolymer or copolymer of a monoolefin(s) of the formula $R'CH=CH_2$ wherein R' is H or an alkyl radical, usually of not more than eight carbon atoms.

With respect to the second major embodiment of the invention, the fluorocarbon polymers (1) and (2) may be added independently to, for example, a hydrocarbon polymer on a rubber compounding mill or in a Banbury or other internal mixer or in a mixing extruder, in all of which the fluorocarbon polymers are uniformly distributed throughout the host polymer. It is also feasible to dry-blend the two fluoropolymers with the host polymer in the solid state, and then effect uniform distribution of the fluoropolymers in the melt extruder employed in the fabrication by using an extruder screw with good mixing capability.

Alternatively, masterbatch dispersions (mixtures) of types (1) and (2) in a diluent polymer, either together or separately, can be metered to the feed section of the extruder by appropriate devices. The diluent polymer can be a difficultly melt-processible polymer, or it can be a compatible melt-processible polymer that does not substantially deleteriously affect the interaction of the aforesaid components (a), (b)(1) and (b)(2) in achieving the beneficial effects of the invention. For example, the diluent polymer can be a melt-processible hydrocarbon polymer, such as a homopolymer or copolymer of a monoolefin(s) of the formula $RCH=CH_2$ wherein R is H or an alkyl radical, usually of not more than eight carbon atoms. In most cases such a hydrocarbon polymer will have a melt index (ASTM D-1238) at 190°C of 20.0 or less, preferably 5.0 or less. In preparing such masterbatches the amounts of fluorocarbon polymers types (1) and (2) will usually be such that they provide 1-25 wt. %, preferably 1-10 wt. %, most preferably 1-5 wt. %, of the masterbatch. Further to the above regarding the need to avoid adversely affecting the beneficial effects of the invention, in preparing the masterbatch, the concentrations of types (1) and (2), as well as the diluent polymer, will be selected so as to achieve good mixing of all the ingredients. Particularly, fibrillation of the fluorocarbon polymer type (2) is to be avoided. In any of the above procedures, it is also possible to employ previously prepared mixtures of fluorocarbon polymer type (1) with fluorocarbon polymer type (2).

In the practice of either major embodiment of this invention, it will be found that the beneficial effects in the reduction of extruder die pressures and improvement in the rates of extrusion that may be employed without encountering melt fracture are not necessarily observed immediately on the onset of extrusion, and depending on the overall concentrations of modifier, it may take from 10 minutes to 8 hours to reach stable extrusion rate and die pressure. Longer times are required at low concentrations of fluoropolymer process aid and with process aids having lower concentrations of the functional group W. When it is desirable to hasten the achievement of equilibrium, it may be expedient to first "condition" the extruder rapidly using a composition containing 0.5-2 parts of the fluoro polymer and then to switch to the desired lower concentration of process aid.

Just as it has been observed that the beneficial effects may not be observed immediately, it has also been observed that the beneficial effects may continue to be observed after addition of the fluorocarbon polymer process aid is discontinued. Consistent with this observation, after stable extrusion rate and die pressure are achieved, the beneficial effects of the invention may be realized by alternating a feed of difficultly melt-processible polymer and one containing the processing aid of the invention.

First Major Embodiment of the Invention

The fluoropolymer process aid of the embodiment of the invention as first described in the Summary should have a high fluorine content, such that the fluorine to carbon ratio is at least 1:2, preferably at least 1:1.5, so that the die-coating film will have a low critical surface energy. Resultantly, there is little wetting of the fluoropolymer by the difficultly-melt-processible resin, and the coated die surface is thereby rendered less resistant to the flow of the polymer melt. In this embodiment it is essential that the fluoropolymer have an effective amount of polar functionality to bond the process aid to the metal or metal oxide die surface through chemical and/or physical interaction. Suitable polar groups include sulfonic or carboxylic groups of the type disclosed hereinbelow, and may be situated on the polymer chain ends as a result of the polymerization procedure or by a post-polymerization treatment step, or they may be randomly located along the polymer chain as part of a polar-group-containing copolymerized monomer.

For example, copolymers of tetrafluoroethylene and hexafluoropropylene having high concentrations of polar polymer chain end groups are excellent process aids for difficultly-melt-processible resins (see Example 1). These polymers are prepared in aqueous polymerization systems using inorganic peroxide initiators that provide -COOH or -COF polymer chain end groups. In contrast, when such polar end groups are removed by a humid heat treatment in isolation, as is common in commercial practice, as disclosed in U.S. Patent 3,085,083, or by a fluorination reaction, as disclosed in U.S.Patent 4,742,122, these compositions no longer function as effective process aids (see Comparative Examples 1 and 2).

Accordingly, the fluoropolymer process aids of this embodiment of the invention have a molecular weight of at least 10,000, have a fluorine to carbon ratio of at least 1:2, preferably at least 1:1.5, are capable of forming a slip layer coating at the die surface and have chain ends bearing one or more functional groups, W, wherein W is selected from -COF, $-OSO_3M$, $-SO_3M$ and -COOM, wherein M is hydrogen, a metal cation, preferably an alkali or alkaline earth metal cation, or a quaternary ammonium cation. The concentration of the functional group, W, should be at least 100 groups per million carbon atoms (pmc), preferably at least 200 groups pmc. It may be advantageous to use in combination more than one of the process aids of the invention. As already recited hereinabove, the concentration of the process aid in the difficultly-melt-processible polymer is 0.002-0.5 wt. %, preferably 0.01-0.2 wt. %.

In one important aspect of this embodiment of the invention, the fluoropolymer process aid is a homopolymer or copolymer of tetrafluoroethylene having a high concentration of polar functional polymer chain end groups that are introduced as a consequence of the polymerization method employed. Such polymers include the following: melt-processible, partially crystalline copolymers of tetrafluoroethylene and 2-20 mole % of at least one perfluoroolefin of 3 to 8 carbon atoms, preferably hexafluoropropylene, prepared, for example, according to U.S. Patent 2,946,763, preferably without a buffer to ensure the presence of -COOH end groups; partially crystalline copolymers of tetrafluoroethylene and perfluoro(alkyl vinyl ether), preferably the propyl vinyl ether, prepared, for example, by an aqueous process according to U.S. Patent 3,635,926 and having, for the most part, -COOH end groups, or by a non-aqueous process, for example, according to U.S. Patent 3,642,742 and having, for the most part, -COF end groups, the disclosures of all of which are incorporated herein by reference. The concentrations of -COF and -COOH groups in such polymers can be measured by the infrared method described hereinbelow.

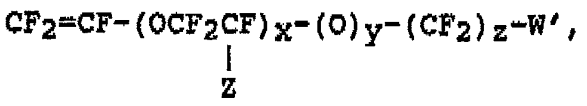
As used herein, the term "partially crystalline" means that the fluoropolymer is melt processible, and has a crystalline melting point above room (ambient) temperature, as distinguished from the uncured fluoroelastomers described below, which will normally have melting points or glass transition temperatures below room (ambient) temperature. Such elastomers are often available as articles of commerce. It is to be understood that small changes of the monomer ratios in such polymers may cause them to have crystallinity that prevents their utility as elastomers, without detracting from their utility as fluoropolymers in the compositions and processes of this invention.

Uncured fluoroelastomers having utility as process aids in the invention include elastomeric copolymers of vinylidene fluoride and one or more fluorine-containing comonomers. Such fluoroelastomers are exemplified by the following: copolymers of vinylidene fluoride and a monomer selected from hexafluoropropylene, chlorotrifluoroethylene, 1-hydropentafluoropropylene and 2-hydropentafluoropropylene; copolymers of vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene or 1- or 2-hydropentafluoropropylene; and copolymers of vinylidene fluoride, hexafluoropropylene and a perfluoro(alkyl vinyl ether). Such copolymers can be prepared in aqueous emulsion polymerization systems using inorganic initiators, such as described in U.S. Patents 2,986,649 and 3,051,677. Other useful fluoroelastomers include perfluoroelastomers comprised of tetrafluoroethylene and a perfluoro(alkyl vinyl ether), preferably perfluoro(methyl vinyl ether), such as are disclosed in U.S. Patents 3,132,123 and 4,281,092. Elastomeric copolymers of tetrafluoroethylene and propylene, optionally with a small amount of vinylidene fluoride, also have utility herein.

Fluoropolymer elastomers that are prepared in aqueous emulsion polymerization systems will have predominantly $-OSO_3H$ and $-COOH$ polymer chain end groups, when thermal initiation is employed, as well as $-SO_3H$ end groups, when redox initiation systems are used. (See Logothetis, Prog. Polym. Sci., Vol. 14, pp 257,258 [1989]). The emulsions can be coagulated by addition of salts, such as sodium chloride, magnesium sulfate or aluminum sulfate, and depending on the pH during isolation, the free acids may be present in admixture with their corresponding metal salts.

In another embodiment of the invention, the fluoropolymer process aid can comprise a tetrafluoroethylene homopolymer or a copolymer of tetrafluoroethylene and a perfluoro monomer selected from hexafluoropropylene and a perfluoro(alkyl vinyl ether), that has been subjected to sufficient ionizing radiation, for example, by a method such as disclosed in U.S. Patent 3,766,031, to provide the end groups necessary to achieve the beneficial effects of the invention. It has been found that this may be achieved by employing, for example, 8-80 megarads, preferably 15-80 megarads, of ionizing radiation. Such treatment generates both -COF and -COOH groups, usually accompanied by at least some backbone scission and reduction in molecular weight. If such ionizing radiation treatment results in substantial crosslinking, the crosslinked fluoropolymer is less desirable as a process aid and, if crosslinking is extensive, it may be inoperable in this invention.

In yet another important embodiment of the invention the fluoropolymer process aid with polymer chain end groups can comprise a copolymer of tetrafluoroethylene and 0.5-40 mole %, preferably 4-40 mole %, of a functional-group-containing monomer



$$CF_2{=}CF\text{-}(OCF_2\underset{\displaystyle Z}{\underset{|}{C}}F)_x\text{-}(O)_y\text{-}(CF_2)_z\text{-}W',$$

wherein Z is -F or $-CF_3$, x is 0 or an integer of 1-4, y is 0 or 1, z is an integer of 1-12, and W' is $-SO_2F$, $-SO_2Cl$ or -COOR, wherein R is C_{1-3} alkyl, such as are described in U.S. Patents 3,282,875, 3,506,635, 3,718,627, 4,065,366, 4,138,426, 4,178,218, 4,487,668 and British Patents 2,053,902, and 1,518,837 or wherein W' is $-SO_3H$ or -COOM wherein M is hydrogen, a metal cation, preferably an alkali metal cation or a quaternary ammonium cation, for example, tetraalkylammonium, and is derivable from the alkyl halides and esters by acid or base hydrolysis. In preferred compositions of this embodiment Z is $-CF_3$, x and y are each 1, z is 1-5, preferably 2, and W' is $-SO_2F$, $-CO_2CH_3$, $-SO_3H$ or -COOM.

A number of critical requirements must be met for the fluoropolymer process aids of this invention to function well. The fluoropolymer must be insoluble in the difficultly-melt-processible resin. In addition, the fluoropolymer must disperse, and remain dispersed, in the resin without coagulation into large agglomerates that cannot be readily coated onto the die surfaces. Furthermore, the process aid must be capable of forming an adhering layer under the extrusion conditions of temperature and pressure in order to form a slip surface on the polymer-contacting regions of the die. In contrast to the teachings of the prior art, the process aid need not necessarily be above its crystalline melting point or glass transition temperature at the process temperature, so long as it is capable of forming a slip layer at the die surface under the shear stress conditions generated in the extrusion, controlled by the viscosity of the difficultly-melt-processible polymer, the extrusion rate and the prevailing temperature. Thus, certain melt-processible polymers and copolymers of tetrafluoroethylene having melting points as much as 40-130°C higher than the process temperatures are good process aids when all other requirements are met. It is also important that the fluoropolymer process aid be thermally and chemically stable at the melt processing temperature of the polymer resin.

On the other hand, standard, commercially available high molecular weight non-melt-processible polytetrafluoroethylene homopolymers, whether dispersion-produced or suspension-produced, are not film-forming under extrusion conditions and, therefore, are not within the scope of this invention.

Although not wishing to be bound by the following, it is postulated that there is an interaction, chemical and/or physical, between the polar end groups or midchain polar structures, if present, and the polymer-contacting metal surfaces of the extruder, particularly within the die land area, thus causing the formation of an adherent die-coating layer of low surface energy fluoropolymer; and that bonding or attraction between polymer and metal occurs at metal-oxygen bonds on the die surfaces.

The concentration of the polar functional groups in the perfluoropolymer process aid of the invention may be determined from the infrared spectrum of compression-molded films, according to the technique described in U.S. Patents 4,742,122 and 3,085,083, as follows:

The quantitative measurement of the number of end groups is obtained using the absorptivities measured on model compounds containing the end groups of interest. The end groups of concern, the wavelengths involved, and the calibration factors determined from model compounds are shown below:

End group	Wavelength, micrometers	Calibration Factor (CF)
$-COF$	5.31	406
$-CO_2H(M)$	5.52	335
$-CO_2H(D)$	5.64	320
$-CO_2CH_3$	5.57	368
$-CONH_2$	2.91	914
$-CF{=}CF_2$	5.57	635
$-CH_2OH$	2.75	2220

M = Monomeric, D = Dimeric

The calibration factor is a mathematical conversion to give end group values in terms of ends per 10^6 carbon atoms. The concentration of each type of end in a polymer film may generally be obtained from this equation:

$$\text{End Groups per } 10^6 \text{ carbon atoms} = \frac{\text{absorbance x CF}}{\text{film thickness}}$$

where film thickness is in millimeters.

Some of the absorbance peaks may interfere with one another when $-CO_2H(D)$, $-CO_2H(M)$, and $-CF{=}CF_2$ ends are all present. Corrections have been developed for the absorbances of $-CO_2H(D)$ (hydrogen-bonded carboxylic acid dimer) and the $-CF{=}CF_2$ ends. These are as follows (where μ is the wavelength in micrometers):

$$\frac{\text{absorbance } 5.46\ \mu - (0.3 \text{ x absorbance } 5.58\ \mu)}{0.91} =$$

the corrected absorbance for $-CO_2H(D)$

$$\frac{\text{absorbance } 5.57\ \mu - (0.3 \text{ x absorbance } 5.58\ \mu)}{0.91} =$$

the corrected absorbance for $-CF{=}CF_2$

The presence of $-CONH_2$ or $-CO_2CH_3$ may also interfere with the acid and $-CF=CF_2$ absorbances. Since these groups are generally the result of additives to polymerization, their presence is generally predictable. A suspicion of $-CONH_2$ absorbance in the vicinity of 5.6 micrometers can be checked by searching for the auxiliary $-CONH_2$ band at 2.91 micrometers.

The polymer films (0.25 to 0.30 mm thick) are scanned on a Perkin-Elmer 283B spectrophotometer with a film of the same thickness, and known to contain none of the ends under analysis, in the instrument reference beam. The instrument is set up with a Response Time setting of 1, a Scan Time setting of 12 minutes, Ordinate Expansion of 2, a Slit Program of 7, and an Auto-Chek Gain control of 20%. The films are then scanned through the pertinent regions of the spectrum making sure that adequate base lines are established on each side of the pertinent absorbances.

The polymer films are generally compression molded at 270°-350°C. The presence of certain salts, particularly alkali metal salts, may cause end group degradation within this temperature range. If these salts are present, the films should be molded at the lowest possible temperature.

Note that this method is calibrated for use with perfluoropolymers. If the carbon to which the functional group is attached contains hydrogens, there will be some shifts in absorption wavelengths and calibration factors, as will be apparent to those skilled in the art.

EXAMPLES

Examples 1-8 that follow were carried out with a C. W. Brabender Instruments, Inc. Computerized Plasti-Corder equipped with a 19.1 mm. (3/4 in.)

diameter extruder with a 25/1 length/diameter ratio. The chromium plated screw had ten feed flights, 10 compression flights with a compression ratio of 3:1, and 5 metering flights. Operating parameters were controlled by four or five independent heating zones, depending on the die, two pressure transducers and a torque-measuring drive unit with 1-120 rpm capability. The instrument was equipped with software for rheometric extrusion testing. One of two die assemblies was used, as noted in the examples, a standard nitrided #416 stainless steel capillary die with a diameter of 2 mm. and L/D of 20, or a horizontal ribbon (tape) die body made of #416 ferritic stainless steel, supplied by C. W. Brabender and designed to accept chromium plated die inserts such that the exit width was 2.54 cm. (1.0 in.), the land length was 1.016 cm. (0.4 in.) and the die gap was a nominal 0.508 mm. (0.02 in.). The various new die inserts were used as received after wiping with ScotchBrite® scouring pads and acetone to remove surface contaminants.

In operation, the required machine conditions were set and the polymer resin then extruded, usually at 40 rpm when using the capillary die, and 60 rpm when using the tape die, until equilibrium (constant throughput and constant die pressure) was reached. Experiments were carried out in a sequence of unmodified resin, followed by resin containing fluoropolymer process aid. When changing the feed composition, the initial output parameters corresponded to the previous equilibrium, and then gradually changed to a new equilibrium. In some of the examples that follow, when switching from unmodified hydrocarbon polymer to the blend containing fluoropolymer process aid, a "conditioning" operation using a 1% blend of fluoropolymer process aid was first used for 30 min. to speed the attainment of equilibrium, and then the feed was switched to a blend containing the desired test concentration of fluoropolymer process aid. Equilibrium was achieved for each composition, and a range of screw speeds was run to produce new equilibrium values of throughput and die pressure. Surface quality of the extrudate was judged by visual examination.

After each series of examples the die inserts were removed, and the die body and extruder were purged with one of several materials, such as PCX-12 purge compound (available from Du Pont Canada), Du Pont 3535 polyethylene 1 melt index linear low density polyethylene (LLDPE), or LLDPE containing 20% silica. Replacement die inserts were installed. After calibration of the transducers, the unmodified resin was run to establish equilibrium conditions, and to assure that reliable output was being obtained. If previously established equilibrium values for unmodified resin were not achieved, the cleanout procedure was repeated. Because combinations of small amounts of fluoroelastomer and fluororesins can act synergistically, the extruder was cleaned extremely well following any use of fluoroelastomer using the following procedure. The extruder and die body were purged as above and then completely disassembled. The screw, barrel, die assembly, transducers and thermocouples were thoroughly cleaned, first with a motor driven brass brush, and finally with acetone solvent. An extrusion test for equilibrium parameter values was then carried out as described above.

The linear low density polyethylene, LLDPE, used in the following examples was a high molecular weight, linear low density (d=0.918) copolymer of ethylene and butene-1 having a melt index (ASTM D-1238, cond. E) of 1.0.

Example 1

(A) To the extruder, equipped with a capillary die, was fed unmodified LLDPE with the screw operating at 40 rpm and heating zones No 1 - 5 controlling at nominal temperature settings of 150, 180, 200 and 204 and 205°C, respectively. Equilibrium extrusion conditions, where throughput and die pressure were constant, were reached after a period of 30 min. The screw speed was then systematically varied from 20 rpm to 120 rpm. After determining the extrusion rate at various screw speeds, the data were used to generate a curve of die pressure vs. throughput such as is shown in Figure 1 as Curve 1. Surface appearance of the die strand was evaluated visually. Melt fracture occurred at all extrusion rates in excess of 8 g./min., the lowest rate attainable on the equipment. For purposes of comparison, "melt fracture" is defined as a herringbone-like roughness on the surface of the extrudates.

(B) Without changing conditions, the extruder feed was changed to a blend containing 0.05 wt. % (500 ppm) of a copolymer (FEP) of tetrafluoroethylene and 12 wt. % of hexafluoropropylene having a melt viscosity of 10.3 x 10^4 poise and a DSC melting point maximum in the range 250-280°C. It was in a powder form, prepared without humid heat treatment during isolation. By infrared analysis it was shown to contain approximately 420 carboxyl end groups per million carbon atoms and had essentially no -COF end groups. The die pressure decreased gradually, and after a total time of 120 min. following the switch to fluoropolymer blend, a new equilibrium was established. Extrusion was continued without any further die pressure changes, and after a total extrusion time of 210 min., a plot of die pressure vs. extrusion rate was generated as shown in Figure 1, Curve 2. Melt fracture did not occur up to a maximum extrusion rate attainable of 52 g/min.

Comparative Example 1

A portion (50 g) of an FEP polymer powder similar to that used in Example 1 was placed in a chamber which was evacuated, purged with nitrogen, and then heated to 95°C. The chamber was again evacuated and pressured back up with nitrogen, evacuated again and then pressured back up with a 25/75 volume mixture of fluorine/nitrogen gases. The temperature was allowed to rise to 100°C and the same gas mixture was passed through the reactor at 0.9 L/min. for 2 hrs. The temperature was raised to 185°C while maintaining the same gas flow. After 1 hr. at 185°C the gas flow rate was decreased to 0.7 L/min. The fluorine/nitrogen flow was maintained at this level for 4 hrs. after the temperature was raised to 185°C. The total amount of fluorine passed through the reactor was calculated from the cylinder pressure change to be 0.8 gram per gram of polymer. The chamber was then purged with nitrogen, cooled to room temperature, and opened to obtain the treated polymer. The treated polymer was cold pressed into a film which was scanned by Infrared Spectroscopy. Using known IR absorptivities for -COF and -COOH structures in fluoropolymers, it was determined that the treated polymer contained 14 -COF ends per million carbon atoms and no -COOH ends. It had a melt viscosity of 9.94×10^4 poise.

LLDPE containing no fluoropolymer additive was extruded as described in Example 1, giving essentially equivalent results. Extrusion of LLDPE containing intimately blended therein 500 ppm of the above fluorine-modified FEP polymer was carried out as in Example 1. There was no drop in die pressure when the modified FEP was introduced, as shown by curve 3 in Figure 1, and there was no improvement in melt fracture behavior compared to the unmodified LLDPE (curve 1).

Comparative Example 2

An FEP polymer was prepared in a fashion similar to that used in the preparation of the FEP sample of Example 1, except that it was subjected to a humid heat treatment in isolation, as described in U.S. Patent 3,058,083. It had a melt viscosity of 7.8×10^4 poise and by infrared analysis had no detectable end groups. A blend of 1000 ppm of this polymer in LLDPE was evaluated as described in Example 1. There was no reduction in die pressure or improvement in melt fracture behavior for the blend, relative to the LLDPE not containing this fluoropolymer.

Comparative Example 3

This experiment was carried out as described in Example 1, except the tape die assembly was used and the four heating zones were controlled at 150, 180, 200 and 204°C, respectively. Using LLDPE not containing fluoropolymer process aid, the Control reference data shown in Figure 2 as Curve 1 were obtained as described in Example 1.

Comparative Example 4

Using the procedures of Comparative Example 3 a blend of LLDPE containing 1000 ppm of intimately dispersed, commercially available, dispersion-process-polymerized, fibrillatible, non-melt-processible polymer of TFE containing a small amount of copolymerized hexafluoropropylene was evaluated; end group functionality was immeasurably low. There was no reduction in extruder die pressure or improvement in melt fracture behavior.

Example 2

Using the procedure of Comparative Example 3 a blend of LLDPE containing 1000 ppm of a high molecular weight, dispersion-produced PTFE, that had been subjected to 60 megarads of ionizing radiation and had 650 -COF and 1235 -COOH end groups per million carbon atoms and a DSC melting point of 321°C, was evaluated. There was a significant reduction in extruder die pressure, compared to the control, as shown in Figure 2, Curve 3, and melt fracture occurred only at extrusion rates above 42 g/min.

Example 3

Using the procedure of Comparative Example 3 a blend of LLDPE containing dispersed therein 200 ppm of a copolymer of tetrafluoroethylene and 13.2 mole % of perfluoro-3,6-dioxa-4-methyl-7-octene sulfonic acid (Aldrich Chemical Co., Cat. No. 27673-1) was evaluated. The plot of die pressure vs. extrusion rate is shown in Curve 2 of Figure 3 and is compared with the unmodified LLDPE control, Curve 1, which was generated in Comparative Example 3. Melt fracture had not occurred at extrusion rates of 48 g/min., the maximum extrusion rate achievable.

Example 4

Using the procedure of Comparative Example 3 a blend of LLDPE containing 200 ppm of the tetrafluoroethylene copolymer of Example 3 and 200 ppm of an FEP copolymer similar to that of Example 1, but having 456 -COF and -COOH end groups per million carbon atoms and a melt viscosity of 8.95 x 10^4 poise, was evaluated. Extrusion data are shown in Curve 3 of Figure 3. Melt fracture had not occurred at an extrusion rate of 49 g/min., the maximum rate achievable.

Example 5

In a procedure like that of Comparative Example 3 a blend of LLDPE containing 400 ppm of a copolymer of tetrafluoroethylene and 13.7 mole % methyl perfluoro(4,7-dioxa-5-methyl-8-noneneoate) and 100 ppm of the FEP copolymer of Example 4 was evaluated. Extrusion data are shown as Curve 4 in Figure 3. Melt fracture did not occur at extrusion rates below 48 g/min., the maximum rate achievable.

Example 6

In a procedure like that of Comparative Example 3 a blend of LLDPE containing 1000 ppm of a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octene sulfonyl fluoride was evaluated. The plot of die pressure vs. extrusion rate is shown in Curve 5 of Figure 3. No melt fracture was observed up to the maximum extrusion rate tested, 53 g/min.

Example 7

A terpolymer having principally sulfonic end groups was prepared in a 4L mechanically agitated, water-jacketed, stainless steel autoclave operating continuously at 70°C and 4800 kPa, into which was pumped, at a rate of 500 mL/h, an aqueous polymerization medium/initiator solution comprised of 500 mL water and 6.7 g sodium sulfite and, at a rate of 600 mL/h, another aqueous solution comprising 600 mL water, 7.5 g ammonium persulfate and 15 g ammonium perfluorooctanoate. At the same time, tetrafluoroethylene (250 g/h), perfluoro(methyl vinyl ether) (325 g/h) and perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octene) (8CNVE, 14.4 g/h) were fed to the autoclave as a compressed mixture at a constant rate by means of a liquid pump. Polymer latex was removed continuously by means of a let-down valve and unreacted monomers were vented. The latex, from about 5 hrs. operation, was added with stirring to a preheated (90°C) coagulating solution consisting of 230 g magnesium sulfate in 25 L water. The coagulated crumb was filtered off, washed repeatedly with water and dried by heating in an air oven at 80°C for 48 hrs. to give about 2300 g of polymer. The polymer composition (wt %) was 63% TFE, 35% PMVE and 2% 8CNVE as determined by infrared analysis.

In a procedure like that of Example 1 a blend of LLDPE containing 1000 ppm of the above-prepared fluoropolymer was evaluated. Extrusion data are shown by Curve 2 of Figure 4 and are compared with data for LLDPE containing no fluoropolymer process aid in Curve 1. Melt fracture did not occur at extrusion rates below 52 g/min., the maximum rate achievable.

Example 8

A terpolymer having principally carboxyl end groups was prepared in a 4L mechanically agitated, water-jacketed, stainless steel autoclave operating continuously at 90°C and 4800 kPa, into which was pumped, at the rate of 1500 mL/h, an aqueous polymerization medium/initiator solution comprising 1500 mL water, 3.85 g ammonium persulfate, 22 g of ammonium perfluorooctanoate ("Fluorad" FC-143, 3M Co.) and 22 g disodium hydrogen phosphate heptahydrate ($Na_2HPO_4.7H_2O$). At the same time, tetrafluoroethylene, TFE, (465 g/h), perfluoro(methyl vinyl ether), PMVE, (480 g/h) and vinylidene fluoride, VF_2, (3.0 g/h) were fed to the autoclave at a constant rate by means of a diaphragm compressor. Polymer latex was removed continuously by means of a let-down valve and unreacted monomers were vented. The latex, from about 4 hrs. operation, was added with stirring to a preheated (90°C) coagulating solution consisting of 320 g magnesium sulfate in 25 L water. The coagulated crumb was filtered off, washed repeatedly with water and dried by heating in an air oven at 80°C for 48 hrs. to give abut 3200 g of polymer. The polymer composition (wt %) was 64.8% TFE, 34.8% PMVE and 0.4% VF_2 as shown by infrared analysis.

In a procedure like that of Example 1 a blend of LLDPE containing 1000 ppm of the above-described fluoropolymer was evaluated. Extrusion data are shown by Curve 3 of Figure 4. Melt fracture did not occur at extrusion rates below 42 g/min., the maximum rate achievable.

Comparative Example 5

In a procedure like that of Comparative Example 3, a blend of LLDPE and 1000 ppm of a commercially available (Du Pont Company) powdered, essentially alternating copolymer of tetrafluoroethylene and ethylene. It had a DSC melting maximum in the range of 250°C. Although acid or acid fluoride end groups of this fluoropolymer were not measured, it is expected that their concentration is very low because of the high hydrocarbon concentration and the method of polymerization of the polymer (see U.S. Patent 3,624,250). There was no die pressure drop relative to that of the LLDPE containing no fluoropolymer process aid, and melt fracture occurred at all extrusion rates above 16 g/min., the minimum rate tested.

Example 9

The equipment employed was a Haake Buchler Rheomix® 19.1 mm (3/4 in.) diameter single-screw extruder with a chromium plated one-stage metering screw having a 20/1 length/diameter ratio, 10 feed flights, 5 compression flights, 5 metering flights and a channel depth ratio of 3. Operating parameters were controlled by four independent heating zones, two pressure transducers and a torque-measuring drive with 1-200 rpm capability. The extruder was equipped with software for rheometric capillary extrusion testing. The capillary die, made from #416 stainless steel, had a diameter of 1.27 mm and a length of 39.1 mm and was previously unused. Prior to each use the extruder was thoroughly cleaned by first purging with linear low density polyethylene containing 20% silica. The extruder was then disassembled and each section was cleaned with a wire brush and then methyl ethyl ketone solvent. The die holder was cleaned by heating at 600°C for 4 hrs.

(A) A commercially available extrusion grade polystyrene, Styron® 685D (Dow Chemical Co.), density 1.40 g/cc, melt flow rate 1.6 g/10 min., was fed to the extruder, equipped with a new die, with the screw operating at 5 rpm and heating zones 1, 2, 3, and 4 controlled at nominal settings of 150, 180, 200 and 204°C, respectively (No. 4 is closest to the die). Equilibrium extrusion conditions were achieved after 120 min. The screw speed was then systematically varied from 1 rpm to 120 rpm to generate, as previously described, the correlation of extruder throughput and die pressure shown in Curve 1 of Figure 5. Melt fracture was not observed at any screw speed tested, but die buildup (collection of polymer at the exit of the capillary die) was observed at screw speeds greater than 60 rpm.

(B) Without changing conditions the feed was changed to a powder blend of polystyrene containing 0.05 wt. % of the irradiated PTFE described in Example 2. Using the procedure of Part A, a new equilibrium was established after 240 min., and the data of Curve 2 of Figure 5 was generated. Die buildup was not observed at any screw speed.

Example 10

In a procedure like that of Example 9, except that the extruder heating zones Nos. 1, 2, 3 and 4 were controlled at nominal temperature settings of 160, 180, 220 and 220°C, respectively, the performance of an extrusion grade ethylene/vinyl acetate copolymer (Du Pont Elvax®-3135), density 0.930 g/cc, melt index of 0.35 g/10 min., was evaluated. Curve 1 of Figure 6 shows data for extrusion of unmodified EVA polymer. Curve 2 shows data for extrusion of a blend containing 0.05 wt. % of a copolymer similar to that of Example 8 but comprised of 55.4 wt. % of tetrafluoroethylene, 44.2 wt. % perfluoro(methyl vinyl ether) and 0.4 wt. % vinylidene fluoride.

Example 11

(A) In a procedure like that of Example 9, except that the extruder heating zones Nos. 1, 2, 3 and 4 were controlled at nominal temperature settings of 280, 310, 310 and 310°C, respectively, the performance of an extrusion grade PET copolymer of ethylene glycol and terephthalic acid (Goodyear Co.), density 1.39 g/cc, inherent viscosity (0.05 wt. % in a 3/1 mixture of methylene chloride and trifluoroacetone) 1.65, was evaluated. Die pressure was measured at a constant screw speed of 5 rpm over a period of 120 min. The die pressure fluctuated steadily between about 3 to 10 MPa over a time period of several minutes. After 120 min. the screw speed was varied from 1 to 30 rpm. Large die pressure fluctuations continued and at 30 rpm caused automatic shutoff of the extruder which had a safety cutoff pressure set at 70 MPa. At 30 rpm flow rate was 19.8 g/min. Thus, the PET could not be extruded at screw speeds greater than 30 rpm or at a flow rate greater than 19.8 g/min. In addition, an accumulation of dark decomposed polymer was observed to build up at the exit of the capillary die at all extrusion speeds.

(B) Without changing conditions, the extruder feed was changed to a powder blend of the PET containing 0.05 wt. % of the fluoroelastomer described in Example 10. After several minutes at 5 rpm the large pressure fluctuations observed above abruptly ceased. After 120 minutes the screw speed was varied from 1 to 60 rpm, where the flow rate was 31.2 g/min. The pressure was steady at all speeds and there was no accumulation of decomposed polymer at the die exit. At 90 rpm the pressure exceeded the safety cutoff pressure.

Example 12

(A) In a procedure like that of Example 9, except that the extruder heating zones Nos. 1, 2, 3 and 4 were controlled at nominal temperature settings of 260, 290, 297 and 297°C, respectively, the performance of a commercially available extrusion grade copolymer of ethylene glycol and terephthalic acid containing 0.25 wt. % trimellitic anhydride, inherent viscosity (0.05 wt. % in a 3/1 mixture of methylene chloride and trifluoroacetone) 1.05, DSC melting point 254°C, was evaluated. Die pressure was measured at a constant screw speed of 5 rpm over a period of 120 min. The die pressure fluctuated steadily between about 3 to 10 MPa over a time period of several minutes. After 120 min. the screw speed was varied from 1 to 60 rpm. Large die pressure fluctuations contined at all speeds. Above 60 rpm pressure fluctuations caused automatic shutoff of the extruder (pressure reached 70 MPa). At 60 rmp the flow rate was 30.6 g/min. Thus, the PET could not be extruded at screw speeds greater than 60 rpm or at a flow rate greater than 30.6 g/min.

(B) Without changing conditions the extruder feed was changed to a powder blend of the same polyester containing 0.05 wt. % of the carboxyl-group-containing FEP copolymer described in Example 1. After several minutes at 5 rpm the large pressure fluctuations observed above abruptly ceased and the die pressure became steady. After 120 minutes the screw speed was varied from 1 to 90 rpm, where the flow rate was 40.8 g/min. and the pressure was steady at all speeds. At 120 rpm the pressure exceeded the safety cutoff pressure.

Comparative Example 6

The procedure of Example 12 was repeated except that in Part B a blend containing 0.05 wt. % of the FEP polymer described in Comparative Example 2 was evaluated. The large pressure fluctuations of Part A were not diminished in the procedure of Part B and continued for a period of greater than 120 minutes at 5 rpm. The screw speed was varied from 1 to 60 rpm, where die pressure fluctuations continued at all speeds. At 60 rpm the flow rate was 26.4 g/min. At 90 rpm the pressure exceeded the safety cutoff pressure of the extruder, 70 MPa.

Example 13

(A) In a procedure like that of Example 9 a commercially available fiber grade nylon 66 having a relative viscosity of 43, density 1.10 g/cc (T-972; Du Pont Co.) was fed into the extruder with the screw operating at 5 rpm and heating zones Nos. 1, 2, 3 and 4 controlled at nominal temperature settings of 260, 270, 270, 270°C, respectively. After steady conditions were achieved, die pressure was measured at a constant screw speed of 5 rpm over a period of 120 minutes, during which time the die pressure fluctuated regularly between about 4.8 to 14 MPa with a time period of several minutes. The screw speed was then systematically varied from 1 rpm to 120 rpm. Large die pressure fluctuations were observed at all screw speeds up to 60 rpm (flow rate of 9.6 g/min.), diminishing to about ± 0.7 MPa at 90 and 120 rpm. Representative extrusion data are shown in Figure 7, Curve 1.

(B) Without changing conditions, the extruder feed was changed to a powder blend of the nylon containing 0.05 weight percent of the irradiated PTFE described in Example 2. After several minutes at 5 rpm the large fluctuations in die pressure observed in the procedure of Part A ceased and the die pressure became steady, with fluctuations of no more than ± 0.15 MPa. Extrusion was continued without any further die pressure change. After 120 min., the screw speed was systematically varied from 1 rpm to 120 rpm. Die pressure was steady at all screw speeds with fluctuations of no more than ± 0.15 MPa. Data are shown in Figure 7, Curve 2.

Example 14

The evaluations reported below employed the apparatus described in Example 9, except for using a capillary die made from #416 nitrided stainless steel that had a diameter of 0.38 mm and a length of 0.76 mm. The die was heated in an electric furnace for 4 hours at 450°C prior to use.

This example is again disclosed as Parts A and B of Example 33, since it also demonstrates the second major embodiment of the invention.

(A) A commercially available fiber grade nylon 66 having a relative viscosity of 43, density 0.10 g/cc (T-972; Du Pont Co.) was fed into the extruder with the screw operating at 5 rpm and heating zones Nos. 1, 2, 3 and 4 controlled at nominal temperature settings of 260, 270, 270 and 270°C, respectively, (No 4 is closest to the die). After equilibrium was achieved, screw speed was reduced to 3 rpm to achieve an extrusion rate of 2 g/min. Die pressure at this extrusion rate was 3.1 MPa. After a period of one hour no buildup of polymer was observed at the exit of the die. The temperatures of heating zones 3 and 4 were then both increased periodically in 5°C increments, up to a temperature of 300°C. In each case the extrusion speed was adjusted to 2 g/min. by changing the rpm, and the extrusion was continued for one hour. Whenever a die deposit was observed to collect at the die exit, at any temperature, the die was cleaned by wiping shortly after increasing to the next higher temperature and adjusting the screw speed. Buildup of a ring of black decomposed polymer first appeared at the exit of the die, around the extruding nylon fiber, during the extrusion at 280°C. Similarly, a ring of decomposed polymer appeared at all temperatures tested between 280° and 300°C.

(B) Starting conditions were returned to a screw speed of 5 rpm and heating zones Nos. 1, 2, 3 and 4 where controlled at settings of 260, 270, 270 and 270°C, respectively. The extruder feed was changed to a powder blend of nylon containing 0.05 wt. % of the same irradiated PTFE as used in Example 2. After equilibrium was achieved, screw speed was increased to 10 rpm to achieve an extrusion rate of 2 g/min. Die pressure at this extrusion rate was 3.8 MPa. After a period of one hour, no buildup of polymer was observed at the exit of the die. The temperatures of heating zones 3 and 4 were then incrementally increased as described in Part A. Buildup of a globule of black decomposed polymer first appeared at the exit of the die, near the extruding nylon fiber, during the extrusion at 285°C. After wiping the die clean, a globule of decomposed polymer appeared at all temperatures tested between 285°C and 300°C.

Example 15

In this example the extrusion of polymer alloy comprised of 50 wt. % Zytel® 101 Nylon 6/6 (Du Pont Co.), 16 parts of a copolymer of ethylene/n-butyl acrylate/glycidyl methacrylate (70.6/28/1.4 wt. ratio), 36 parts of an ethylene/n-butyl acrylate/methacrylic acid copolymer (65/25/10 wt. ratio) and containing 1 wt. % zinc stearate and 1.5 wt. % Irganox® 109B antioxidant was evaluated. The alloy was prepared by mixing in a twin-screw extruder at 285°C, 110 rpm, followed by pelletization and then drying to 0.15 wt. % or less of moisture. An extruder similar to that described in Example 9 with a single hole die set at a 45 degree exit angle was employed. With the system operating at 290°C and polymer fed at 60 rpm, a dark ring of degraded polymer formed around the extrudate within a few minutes after extrusion began and slowly increased in size. Parts of the ring periodically broke away and formation of a new ring of degraded material formed again.

Without changing conditions a dry blend of the same alloy containing 0.05 wt. % of the FEP polymer described in Example 1 was fed to the extruder. The ring of degraded polymer gradually decreased in size until after 1.25 hrs. the die face was clean and a clean extrudate was observed. The feed was then changed to a blend of the alloy containing 0.05 wt. % of the irradiated PTFE described in Example 2. There was an approximately 20% drop in die pressure and the extruder die remained free of degraded polymer deposits.

When the extruder feed was changed back to the polymer alloy not containing a fluoropolymer additive, the die pressure increased and a ring of degraded polymer soon formed at the die exit orifice.

Example 16

Using the polymer alloy described in Example 15 an injection blow molding trial was carried out with the parison die nozzle regulated at 280°C. In the absence of fluoropolymer additive there was a black die deposit buildup and deposition of the deposit onto the parison tube. There was no die deposit or contamination of the parison when a dry blend of the alloy containing 0.05 wt. % of the irradiated PTFE of Example 2 was used.

Second Major Embodiment of the Invention

In accordance with the second embodiment of the invention described in the Summary, it has been discovered that for the improvement of extrusion behavior, difficultly melt-processible polymers which contain combinations of fluorocarbon polymers (hereinafter called type (1) fluorocarbon polymers) that are above their melting points if crystalline, or above their glass transition temperatures if amorphous, and are thus molten and fluid at the polymer-processing temperatures, and crystalline or amorphous fluorocarbon polymers (herinafter called type (2) fluorocarbon polymers) that are solid at the polymer melt-processing temperatures, have significant advantage over such difficultly melt-processible polymers which contain equivalent, or even greater, amounts of extrusion-modifying additives of the art, as in U.S. 3,125,547 (supra).

The fluorocarbon polymers of type (1) are those that are fluid at the melt-processing temperature of the difficultly melt-processible polymer. Thus, at processing temperature they must be above their melting points if crystalline, or above their glass transition temperatures if amorphous, preferably no more than 300°C, more preferably no more than 200°C. The polymers should have sufficiently high molecular weight, with number average molecular weights greater than about 10,000, such that they do not exude from the difficultly melt-processible polymer extrudate at melt-processing temperatures. With respect to their chemical composition, it is preferred, but not essential, to employ fluorocarbon polymers having a fluorine to hydrogen ratio of at least 1:1.5. Fluorinated monomers which give rise to suitable polymers include vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene, tetrafluoroethylene and perfluoroalkyl perfluorovinyl ethers. Specific examples of the fluorocarbon polymers of type (1) that may be employed in this invention include copolymers of vinylidene fluoride and a monomer selected from hexafluoropropylene, chlorotrifluoroethylene, 1-hydropentafluoropropylene and 2-hydropentafluoropropylene; copolymers of vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene or 1- or 2-hydropentafluoropropylene; copolymers of tetrafluoroethylene and propylene and, optionally, vinylidene fluoride; copolymers of tetrafluoroethylene and a perfluoro(alkyl vinyl ether), preferably perfluoro(methyl vinyl ether), optionally containing a small amount (up to 2 mole %) of a third monomer; and copolymers of tetrafluoroethylene and hexafluoropropylene, all of which are known in the art. The presence or absence of the third monomer is of no known consequence in this invention. In some cases these copolymers may also include a bromo-containing cure site monomer as taught in Apotheker and Krusic, U.S. 4,035,565, or terminal iodo-groups, as taught in U.S. 4,243,770. The latter patent also discloses the use of iodo group-containing fluoroolefin comonomers. When certain molar ratios of monomers are used in these copolymers, then the glass transition temperature is near or below 0°C; many of these polymers are useful elastomers that are readily available articles of commerce.

The fluorocarbon polymers of type (2) that are solid at the melt processing temperature of the difficultly melt-processible polymer include homopolymers of tetrafluoroethylene and copolymers of tetrafluoroethylene with certain copolymerizable monomers. The selection of the fluorocarbon polymer of type (2) is not limited to high molecular weight polymers, whether the polymer is melt-processible or not melt-processible, whether the polymer is made by dispersion polymerization or suspension polymerization, or how much comonomer is present, except as stated above. For example, if excessive amounts of comonomer are used, the polymer will not be a solid at the temperature used for melt processing the difficultly melt-processible polymer; or, if a copolymer has too low a molecular weight, the copolymer may not be a solid at the temperature used for melt processing the difficultly melt-processible polymer. Suitable tetrafluoroethylene homopolymers include those that are high molecular weight and fibrillate, or do not fibrillate to a substantial extent, under shearing conditions, as well as those which are low molecular weight and non-fibrillating, such as those which have been subjected to ionizing radiation. Suitable monomers copolymerizable with tetrafluoroethylene to give melt-processible copolymers are ethylene, perfluoroolefins such as hexafluoropropylene, and perfluoro(alkyl vinyl ethers) such as perfluoro(propyl vinyl ether) and perfluoro(alkyl vinyl ethers) which contain functional groups such as $-SO_2F$ or $-COOCH_3$. More than one comonomer may be used, provided all the aforesaid requirements are met.

In certain instances, when the difficultly-melt-processible polymer is processed at a high temperature, for example, a polyester or polyamide, some type (2) fluorocarbon polymers, for example, tetrafluoroethylene/hexafluoropropylene copolymers, may also serve as a type (1) fluorocarbon polymer.

The effect of the combined addition of fluorocarbon polymers types (1) and (2) in eliminating roughness of the extrudate, allowing increases in extrusion speed and reducing die pressures is significantly greater than when either type (1) or type (2) is used alone at concentrations equal to the sum of the concentrations of (1) and (2). In some cases it has been shown also that combining types (1) and (2), at total concentrations equal to or greater than that of the combined concentrations of additives, also produces unexpected improvements in certain extrusion parameters, for example, reduction or elimination of die pressure fluctuations, reduction of deposits at the die exit, reduction in the pressure required to operate the screw of the extruder, resulting in an increase in the time an extrusion can be carried out or in an increase in the throughput of polymer. It has been found in some instances that even when (1) and (2) are added at total concentrations as low as 0.0025 wt. %, all extrudate roughness is eliminated at extrusion shear rates well beyond 1000 sec^{-1} (Example 18). Quantities in excess of 1 wt. % are not necessary. In general, if the fluorocarbon polymers are not compatible with the difficultly melt-processible polymer, that is to say, are not soluble in such polymer, the addition of higher levels serves no useful purpose, and when the incompatible fraction becomes too large, it may adversely affect the optical properties of the extrudate. Such is the case, for example, when the difficultly melt-processible polymer is a hydrocarbon polymer. The beneficial effects of even very low ratios of types (1) to (2) or types (2) to (1) are readily evident but, in general, there will be an optimum ratio of types (1) to (2) which may be determined experimentally for any particular combination of types (1) and (2). The weight ratio of fluorocarbon polymer type (1) to fluorocarbon polymer type (2) may vary from 2/98 to 95/5, preferably from 10/90 to 90/10.

Except where noted, the evaluations reported below employ a C. W. Brabender Computerized Plasti-Corder equipped with a 19.1 mm (3/4 in.)

diameter extruder with a 25/1 length/diameter ratio. The screw has ten feed flights, 10 compression flights with a compression ratio of 3:1, and 5 metering flights. Operating parameters are controlled by five independent heating zones (No. 5 closest to the die), four pressure transducers and a torque-measuring drive unit with 1-120 rpm capability. The instrument is equipped with software for rheometric capillary extrusion testing. The capillary die, made from #416 nitrided stainless steel, has a diameter of 2 mm and a length of 40 mm, unless otherwise noted. In operation, the required machine conditions are set and the polymer is then extruded, usually at 40 rpm, until equilibrium (constant throughput and constant die pressure) is reached. For a linear low density polyethylene with a melt index at 190°C of 1, extrusion at 40 rpm at 204°C gives a throughput of about 19-20 g/min. and a die pressure of 28 MPa (Comparative Example 7). For experiments that are run in sequence, by changing the feed composition, the initial output parameters correspond to the previous equilibrium, and then gradually change to a new equilibrium. When equilibrium is achieved a range of screw speeds is then run to produce new equilibrium values of throughput and die pressure. The relation between throughput and die pressure is determined from a plot of the data, and die pressure data at certain fixed production rates can be estimated for comparison of data between experiments. Surface quality of the extrudate is judged by visual examination.

After each run the extruder is thoroughly cleaned. The equipment is first purged with a highly filled abrasive composition, for example, the commercially available UCC-DFD-0964 (Union Carbide Corp.). The capillary die is removed and heated with a propane torch until it is free of polymer and has reached a red glow. The extruder is disassembled and each section - screw, barrel, die assembly, and transducers - is cleaned, first with a wire brush, and then with methyl ethyl ketone solvent. After reassembly and calibration of the transducers, the unmodified hydrocarbon polymer is run first to establish equilibrium conditions, and to assure that reliable output is being obtained. For this purpose, the equilibrium value at 40 rpm, only, was sometimes used. If previously established equilibrium values for unmodified polymer are not achieved, the cleanout procedure is repeated.

In Table 1 which follows the examples the various materials used in the examples are identified.

Comparative Example 7

Hydrocarbon Polymer A was introduced to the extruder with the screw operating at 40 rpm and heating zones Nos. 1, 2, 3, 4 and 5 controlling at nominal temperature settings of 150, 180, 200, 204, and 204°C, respectively (No. 5 is closest to the die). Equilibrium extrusion conditions, when throughput and die pressure were constant, were reached after a period of 15 min. The screw rpm was then systematically varied from 12 rpm to 60 rpm. After determining the extrusion rate at various screw speeds, the data were input to a computer program which generated a curve of die pressure vs. throughput (shown in Curve 1 of Figure 8 which is a part of this specification). Selected values taken from Curve 1 are shown in Table 2. The extrudates of Hydrocarbon Polymer A had surface roughness at all extrusion rates above about 4 g/min.

Comparative Example 8

Hydrocarbon Polymer A which, as a dry blend, had intimately dispersed therein 0.1% of Fluorocarbon Polymer 2A, was added to the extruder just at the end of Comparative Example 1, at the same nominal temperature settings and at a screw speed of 40 rpm. Steady state was achieved after 10 min. and did not change after a further 240 min. The die pressure/throughput relationship was then obtained as in Comparative Example 7 and is shown in Curve 2 of Figure 8. Data are shown in Table 2. There was no significant effect of Fluorocarbon Polymer 2A, alone, on the flow characteristics of Hydrocarbon Polymer A, and surface roughness appeared at all extrusion rates above about 4 g/min.

Comparative Example 9

An extruder warm-up was carried out as in Comparative Example 7 with unmodified Hydrocarbon Polymer A, giving the same results. Hydrocarbon Polymer A which, as a dry blend, had intimately dispersed therein 0.02 wt. % of Fluorocarbon Polymer 1A, was then added to the extruder at the same temperature settings and at a screw speed of 40 rpm. Steady state was achieved after 60 min. and did not change after a further 60 min. The die pressure/throughput relationship was then obtained as in Comparative Example 7 and is shown as Curve 3 in Figure 8. Representative data are shown in Table 2. In this case there was an approximate 10% reduction in die pressure at a given throughput, compared to Comparative Example 7, and extrudates were smooth and glossy at extrusion rates below about 30 g/min.

Example 17

An extruder warm-up was carried out as in Comparative Example 7, giving the same results. Hydrocarbon Polymer A which, as a dry blend, had intimately dispersed therein 0.01 wt. % of Fluorocarbon Polymer 1A and 0.01 wt. % of Fluorocarbon Polymer 2A was then added at the same temperature settings and a screw speed of 40 rpm. A new equilibrium was established, after 180 min., at much lower pressures than for the hydrocarbon resin alone or for the composition of Comparative Example 9. The die pressure/throughput curve was then obtained as in Comparative Example 7, and is shown as Curve 4 in Figure 8. Representative data are shown in Table 2. There was an approximately 30% drop in die pressure over the entire range, compared to Hydrocarbon Polymer A, even though the combined concentrations of Fluorocarbon Polymers 1A and 2A in this example is no greater than the concentration of Fluorocarbon Polymer 1A in Comparative Example 9. Extrudate surfaces were smooth and glossy throughout the range of extrusion rates attainable under the conditions of the example (up to 55 g/min., which is equivalent to a shear rate of about 1500 sec^{-1}). When a 1.5 mm diameter die was used in order to obtain shear rates up to about 3000 sec^{-1}, the extrudate was smooth and glossy over the entire range of extrusion rates.

Example 18

An extruder warm-up was carried out as in Example 17, with similar results. A dry blend of Hydrocarbon Polymer A having intimately dispersed therein 0.0005 wt. % of Fluorocarbon Polymer 1A and 0.0020 wt. % of Fluorocarbon Polymer 2A was then added at the same temperature settings and a screw speed of 40 rpm. The new equilibrium was established after 180 minutes, at a lower die pressure than for the hydrocarbon resin alone or for the composition of Comparative Example 9. The die pressure/extrusion rate curve was obtained as in Example 17 and representative data are shown in Table 2. There was an approximately 28% reduction in die pressure over the entire extrusion rate range compared to Hydrocarbon Polymer A, even though the combined concentrations of Fluorocarbon Polymers 1A and 2A is only 12.5% of the concentration of Fluorocarbon Polymer 1A in Comparative Example 9. Extrudate surfaces were smooth and glossy at extrusion rates below 55 g/min.

Example 19

In this example a series of compositions was evaluated to demonstrate the effect of the relative weight ratios of Fluorocarbon Polymer 1A to Fluorocarbon Polymer 2A, as shown in Table 3. Each composition was a dry blend of Fluorocarbon Polymers 1A and 2A in Hydrocarbon Polymer A, and after extruder warm-up as described in Example 17, each was added at the same temperature settings and a screw speed of 40 rpm. New equilibria were then established after 180 minutes, at lower die pressures than for the hydrocarbon resin alone or for the composition of Comparative Example 9. Die pressure/extrusion rate data were obtained as in Example 17 and are shown in Table 3. There is a significant reduction in die pressure over the entire range compared to Hydrocarbon Polymer A, even though the combined concentrations of Fluorocarbon Polymers 1A and 2A is no greater than the concentration in Comparative Example 9. Extrudate surfaces were smooth and glossy at extrusion rates up to 55 g/min.

Example 20

A composition of Hydrocarbon Polymer A containing an intimate dry powder mix of Fluorocarbon Polymers 1B and 2A, 0.01 wt. % of each, based on difficultly melt-processible polymer, was extruded and evaluated as in Example 17. A control experiment in which the difficultly melt-processible polymer contained 0.04 wt. % of Fluorocarbon Polymer 1B, alone, was also carried out. Data in Table 4 show that the composition of this invention extrudes at very much lower die pressures than the control and the extrudate is free of surface imperfections at much higher extrusion rates, even though it contains only half as much total modifier.

Example 21

A composition of Hydrocarbon Polymer A containing an intimate dry powder mix of Fluorocarbon Polymers 1C and 2A, 0.01 wt. % of each, based on hydrocarbon polymer, was extruded and evaluated as in Example 17. A control experiment in which the hydrocarbon polymer contained 0.04 part by wt. of Fluorocarbon Polymer 1C, alone, was also carried out. Data in Table 4 show that the composition of this example extrudes at very much lower die pressures than the control and the extrudate is free of surface imperfections at much higher extrusion rates, even though it contains only half as much total modifier.

Examples 22 and 23

For each example, Hydrocarbon Polymer A, which as a dry blend had intimately dispersed therein 0.01 wt. % of Fluorocarbon Polymer 1A and 0.01 wt. % of Fluorocarbon Polymers 2B and 2F (Examples 22 and 23, respectively), was added to the extruder and treated in the manner described in Example 17. As shown by the data in Table 5, the new equilibria were then established after 180 minutes, at lower pressures than for the controls represented by Comparative Examples 7 and 9, Table 2. All extrudate surfaces were smooth and glossy throughout the range of extrusion rates up to 38 g/min. Compositions of Hydrocarbon Polymer A and 0.10 wt. % of any of the Fluorocarbon Polymers 2B and 2F showed no improvement in extrusion behavior (data not shown).

Examples 24 and 25

In these examples Hydrocarbon Polymers B and C were compared in formulations containing dry blends of Fluorocarbon Polymers 1A and 2A in the amounts shown in Table 6. Die pressure/extrusion rate data were evaluated as outlined in Example 17. For each example there is a control sample containing no additives and another showing the effect of Fluorocarbon Polymer 1A alone. Data were analyzed as in Example 17 and are shown in Table 6.

Example 26

In this experiment a chrome-plated, 2.54 cm (1 in.) wide slit die having a gap of 0.76 mm (0.03 in.) and a land length of 1.27 cm (0.5 in.) was used. A dry blend composition of Hydrocarbon Polymer A and 0.01 wt. % of each of Fluorocarbon Polymers 1A and 2A was fed at 60 rpm, giving the initial throughput and die pressure ratings indicated in Table 7. The initial extrudate had a rough dull surface. After 3 h the extrudate was smooth and glossy and there was a 17.5% reduction in die pressure as well as a 3.5% increase in throughput. The extrudate surface remained excellent up to the maximum throughput achievable with the extruder (55 g/min. at 120 rpm). In a similarly-run control experiment with Hydrocarbon Polymer A alone, the starting and final parameters were as shown in Table 7, and the extrudate had a dull rough surface at all extrusion rates above about 8 g/min. In another control experiment with 0.02 wt.% of Fluorocarbon Polymer 1A, there was only a 3% pressure drop after 3 h and nil increase in throughput. The extrudate surface was smooth and glossy at 60 rpm, but dull and rough in appearance at all higher screw speeds.

Example 27

The equipment employed was a Haake Buchler Rheomix® 19.1 mm (3/4 in.) diameter single-screw extruder with a chromium plated one-stage metering screw having a 20/1 length/diameter ratio, 10 feed flights, 5 compression flights, 5 metering flights and a channel depth ratio of 3. Operating parameters were controlled by four independent heating zones, two pressure transducers and a torque-measuring drive with 1-200 rpm capability. The extruder was equipped with software for rheometric capillary extrusion testing. The capillary die, made from #416 stainless steel, had a diameter of 1.27 mm and a length of 39.1 mm and was previously unused. Prior to each use the extruder was thoroughly cleaned by first purging with Hydrocarbon Polymer A containing 20% silica. The extruder was then disassembled and each section was cleaned with a wire brush and then methyl ethyl ketone solvent. The die holder was cleaned by heating at 600°C for 4 hrs.

(A) A commercially available extrusion grade polystyrene, Styron 685D (Dow Chemical Co.), density 1.40 g/cc, melt flow rate 1.6 g/10 min., was fed to the extruder, equipped with a new die, with the screw operating at 5 rpm and heating zones 1, 2, 3, and 4 controlled at nominal settings of 150, 180, 200 and 240°C, respectively (No. 4 is closest to the die). Equilibrium extrusion conditions were achieved after 120 min. The screw speed was then systematically varied from 1 rpm to 120 rpm to generate, as previously described, the correlation of extruder throughput and die pressure shown in Curve 1 of Figure 9. Melt fracture was not observed at any screw speed tested, but die buildup (collection of polymer at the exit of the capillary die) was observed at screw speeds greater than 60 rpm.

(B) Without changing conditions the feed was changed to a powder blend of polystyrene containing 0.05 wt. % of Fluorocarbon Polymer 2G. Using the procedure of Part A, a new equilibrium was established after 240 min., and the data of Curve 2 in Figure 9 was generated. Die buildup was not observed at any screw speed.

(C) Without changing conditions the extruder was thoroughly purged with Hydrocarbon Polymer A containing 20 wt. % of silica. Then the procedure of Part A was repeated except that the extruder feed was changed to a powder blend of polystyrene containing 0.05 wt. % of Fluorocarbon Polymer 1D. After a total extrusion time of 250 min., conventional capillary rheometer curves were generated and the plot of Figure 9, Curve 3 was obtained. No melt fracture or die buildup was observed.

(D) The procedure of Part C was repeated except that after purging the feed was changed to a powder blend of polystyrene containing 0.05 wt. % each of Fluorocarbon Polymers 1D and 2G. After a total extrusion time of 240 min. the data shown in Figure 9, Curve 4 was obtained. No melt fracture or die buildup was observed.

Example 28

In a procedure like that of Example 27, except that the extruder heating zones Numbers 1, 2, 3 and 4 were controlled at nominal temperature settings of 160, 180, 220 and 220°C, respectively, the performance of an extrusion grade ethylene/vinyl acetate copolymer Elvax®-3135 (Du Pont Co.), density 0.930 g/cc, melt index of 0.35 g/10 min., was evaluated. Curve 1 of Figure 10 shows data for extrusion of unmodified EVA copolymer. Curve 2 shows data for a blend containing 0.05 wt. % of Fluorocarbon Polymer 2G and Curve 3 shows data for a blend containing 0.05 wt. % of Fluorocarbon Polymer 1D. Curve 4 of the figure show the data for an EVA containing 0.05 wt. % each of Fluorocarbon Polymers 1D and 2G.

Example 29

(A) In a procedure like that of Example 27, except that the extruder heating zones Numbers 1, 2, 3 and 4 were controlled at nominal temperature settings of 280, 310, 310 and 310°C, respectively, the performance of an extrusion grade copolymer of ethylene glycol and terephthalic acid (Goodyear PET), density 1.39 g/cc, inherent viscosity (0.05 wt. % in a 3/1 mixture of methylene chloride and trifluoroacetone) 1.65, was evaluated. Die pressure was measured at a constant screw speed of 5 rpm over a period of 120 min. The die pressure fluctuated steadily between about 3 to 10 MPa with a time period of several minutes. After 120 minutes the screw speed was varied from 1 to 30 rpm. Large die pressure fluctuations continued and at 30 rpm caused automatic shutoff of the extruder, which had a safety cutoff pressure set at 70 MPa. At 30 rpm flow rate was 19.8 g/min. Thus, the PET could not be extruded at screw speeds greater than 30 rpm or at a flow rate greater than 19.8 g/min. In addition, an accumulation of dark decomposed polymer was observed to build up at the exit of the capillary die at all extrusion speeds.

Curve 1 of Figure 11 shows data for the extrusion of unmodified PET up to the point of automatic shutoff. Pressure values are the averages of the high and low extremes.

(B) Without changing conditions, the feed was switched to a blend of the PET containing 0.05 wt. % of Fluorocarbon Polymer 2G; the blend was evaluated as in Part A. After several minutes at 5 rpm the large pressure fluctuations abruptly ceased and there were no pressure fluctuations at screw rates up to 60 rpm, where the flow rate was 28.2 g/min., and there was no accumulation of polymer at the die exit. At 90 rpm high pressure fluctuations again caused automatic shutdown of the extruder. Extrusion data are shown in Curve 2 of Figure 11 and show that, at equivalent flow rates, the extrusion pressures are higher for the blend containing the process aid.

(C) The extruder feed was changed to a powder blend of the PET containing 0.05 wt. % of Fluorocarbon Polymer 1D; the blend was evaluated as in Part A. After several minutes at 5 rpm the large pressure fluctuations observed in Part A ceased. After 120 minutes the screw speed was varied from 1 to 60 rpm, where the flow rate was 31.2 g/min. The pressure was steady at all speeds and there was no accumulation of decomposed polymer at the die exit. At 90 rmp the pressure exceeded the safety cutoff pressure. Extrusion data are shown in Curve 3 of Figure 11. As in Part B, the extrusion pressures were higher for the blend than for the PET not containing process aid.

(D) The procedure of Part A was repeated using a powder blend of PET containing 0.05 wt. % each of Fluorocarbon Polymers 1D and 2G. In this case the extrusion could be carried out at up to 90 rpm without pressure fluctuations, at which rpm a flow rate of 47.4 g/min. was achieved without die accumulation. Moreover, using the combination of process aids the extrusion pressure was surprisingly much lower than when these fluorocarbon polymers were used singly. Data are shown in Curve 4 of Figure 11.

Example 30

The evaluations reported below employed the apparatus described in Example 27, using a capillary die made from #416 nitrided stainless steel that had a diameter of 0.38 mm and a length of 0.76 mm. The die was heated in an electric furnace for 4 hours at 450°C prior to use.

(A) A commercially available fiber grade nylon 66 having a relative viscosity of 43, density 0.10 g/cc (T-972; Du Pont Co.) was fed into the extruder with the screw operating at 5 rpm and heating zones Nos. 1, 2, 3 and 4 controlled at nominal temperature settings of 260, 270, 270 and 270°C, respectively, (No 4 is closest to the die). After equilibrium was achieved, screw speed was reduced to 3 rpm to achieve an extrusion rate of 2 g/min. Die pressure at this extrusion rate was 3.1 MPa. After a period of one hour no buildup of polymer was observed at the exit of the die. The temperatures of heating zones 3 and 4 were then both increased periodically in 5°C increments, up to a temperature of 300°C. In each case the extrusion speed was adjusted to 2 g/min. by changing the rpm, and the extrusion was continued for one hour. Whenever a die deposit was observed to collect at the die exit, at any temperature, the die was cleaned by wiping shortly after increasing to the next higher temperature and adjusting the screw speed. Buildup of a ring of black decomposed polymer first appeared at the exit of the die, around the extruding nylon fiber, during the extrusion at 280°C. Similarly, a ring of decomposed polymer appeared at all temperatures tested between 280° and 300°C.

(B) Starting conditions were returned to a screw speed of 5 rpm and heating zones Nos. 1, 2, 3 and 4 where controlled at settings of 260, 270, 270 and 270°C, respectively. The extruder feed was changed to a powder blend of nylon containing 0.05 wt. % of the same irradiated PTFE as used in Example 2. After equilibrium was achieved, screw speed was increased to 10 rpm to achieve an extrusion rate of 2 g/min. Die pressure at this extrusion rate was 3.8 MPa. After a period of one hour, no buildup of polymer was observed at the exit of the die. The temperatures of heating zones 3 and 4 were then incrementally increased as described in Part A. Buildup of a globule of black decomposed polymer first appeared at the exit of the die, near the extruding nylon fiber, during the extrusion at 285°C. After wiping the die clean, a globule of decomposed polymer appeared at all temperatures tested between 285°C and 300°C.

(C) The procedure of Part A was repeated except that the extruder feed was changed to a powder blend of the nylon containing 0.05 wt. % of an additive similar to Fluorocarbon Polymer 2C but having a melt viscosity of 10,300 Ns/m^2 at 372°C (DSC melting point maximum at 260°C). After equilibrium was achieved at a melt temperature of 270°C and a screw speed of 5 rpm, screw speed was held constant at 5 rpm to achieve an extrusion rate of 2 g/min. Die pressure at this extrusion rate was 4.7 MPa. After a period of one hour no buildup of polymer was observed at the exit of the die. The temperatures of heating zones 3 and 4 were then both increased periodically in 5°C increments as described in Part A, and the extrusion speed was adjusted to 2 g/min. in each case. Buildup of a globule of black decomposed polymer first appeared at the exit of the die, near the extruding nylon fiber, during the extrusion at 280°C, and then at all temperatures tested between 280° and 300°C.

(D) The procedure of Part A was repeated except that the extruder feed was changed to a powder blend of the nylon containing 0.02 wt. % each of the fluorocarbon polymers described in Parts B and C. After equilibrium was achieved at a melt temperature of 270°C and a screw speed of 5 rpm, screw speed was held constant at 5 rpm to achieve an extrusion rate of 2 g/min. Die pressure at this extrusion rate was 4.7 MPa. After a period of one hour no buildup of polymer was observed at the exit of the die. The temperatures of heating zones 3 and 4 were then both increased periodically in 5°C increments to 300°C as described in Part A. No buildup of either a ring or globule of decomposed polymer appeared at the exit of the die during extrusion at any temperature between 270°C and 300°C, the highest temperature tested.

TABLE 1

Type (1) Fluorocarbon Polymers:

1A: A commercially available fluoroelastomer containing polymer repeat units of 60 wt. % vinylidene fluoride and 40 wt. % hexafluoropropylene and having a Mooney viscosity of 60 at 100°C. It was in the form of a fine powder which had been obtained by cryogenic grinding and had a light dusting of calcium carbonate as an antiblocking agent.

1B: A commercially available fluoroelastomer containing polymer repeat units of 45 wt. % vinylidene fluoride, 30 wt. % hexafluoropropylene and 25 wt. % tetrafluoroethylene and having a Mooney viscosity of 80 at 121°C. It was ground and dusted as in 1A.

1C: A commercially available copolymer composed of polymer repeat units of tetrafluoroethylene, propylene and vinylidene fluoride.

1D: A fluoroelastomer containing polymer repeat units of tetrafluoroethylene (55.4 wt. %), perfluoro(methyl vinyl ether) (44.2 wt. %), and vinylidene fluoride (0.4 wt. %).

Type (2) Fluorocarbon Polymers:

2A: A commercially available free-flowing PTFE powder comprising loose agglomerates of sub-micron size particles having fibrillating characteristics that was treated with ionizing electron beam

TABLE 1 (Continued)

radiation until the melt viscosity was reduced to 1.1 x 10^4 Ns/m^2.

2B: A commercially available, high molecular weight, non-melt-processible PTFE, prepared by suspension polymerization, having a standard specific gravity of 2.16 and an average particle size of 35 micrometers.

2C: A commercially available powdered copolymer of tetrafluoroethylene and 12 wt. % of hexafluoropropylene and having a melt viscosity of 9,500 Ns/m^2 at 372°C.

2D: A commercially available powdered copolymer of tetrafluoroethylene and 3-4 wt. % of perfluoro(propyl vinyl ether) and having a melt viscosity of 4,700 Ns/m^2 at 372°C.

2E: A commercially available powdered copolymer of tetrafluoroethylene and 3-4 wt. % of perfluoro(propyl vinyl ether) and having a melt viscosity of 34,000 Ns/m^2 at 372°C.

2F: A commercially available powdered, essentially alternating copolymer of tetrafluoroethylene, ethylene and a small amount of a proprietary comonomer, and having a melt flow of 20 at 297°C (ASTM-D3159).

2G: An experimental polymer sililar to 2A but having a melt viscosity of 11.3 Ns/m^2.

Hydrocarbon Polymers

A: A high molecular weight, linear low density (d=0.918) copolymer of ethylene and butene-1 having a melt index (ASTM D-1238, cond. E) of 1.0.

B: A high density polyethylene (d=0.945) having a melt index of 0.05.

C: A low density (d=0.925) polyethylene containing 5 wt. % of high density polyethylene and a small quantity of poly(vinyl acetate), and having a melt index of 0.50.

TABLE 2

EXAMPLES	-----Comparative Examples-----			Example	Example
	7	8	9	17	18
COMPOSITION (% by wt.)					
Hydrocarbon Polymer A	100	99.9	99.95	99.98	99.9975
Fluorocarbon Polymer 2A	--	0.1	--	0.01	0.002
Fluorocarbon Polymer 1A	--	--	0.02	0.01	0.0005
Throughput (g/min.)	----------------------Die Pressure (MPa)------------				
2.1	9.9				
5.0	16.4			11.7	
7.9	20.4	20.2	18.6	14.3	
10.0	22.1	22.1	19.6	15.6	14.9
15.0	26.3	26.3	24.1	18.9	18.0
20.0	29.1	29.1	27.0	21.1	20.2
25.0	31.3	31.3	29.5	23.4	22.4
30.0	33.5	33.4	31.7	25.4	24.5
35.0	34.3		33.7	26.9	
40.0	35.4			28.3	
45.0	35.8			29.4	
50.0				30.4	
55.0				30.9	
Surface	R, D above 4 g/min.	R,D above 4 g/min.	S,G at 29 g/min. and below	S,G to 55 g/min.	S, G to 55 g/min.

S - smooth
G - glossy
R - rough
D - dull

TABLE 3

	EXAMPLE 19					
	A	B	C	D	E	F
COMPOSITION (% by wt.)						
Hydrocarbon Polymer A	99.980	99.980	99.980	99.980	99.980	99.980
Fluorocarbon Polymer 2A	0.0196	0.019	0.018	0.016	0.002	0.001
Fluorocarbon Polymer 1A	0.0004	0.001	0.002	0.004	0.018	0.019
Wt. ratio 1A/2A	2/98	5/95	10/90	20/80	90/10	95/5
Throughput (g/min.)	Die Pressure (MPa)					
10	15.1	7.7	8.4	11.5	18.3	17.3
15	18.5	9.9	10.7	14.2	21.8	21.1
20	21.0	11.8	13.1	16.3	24.6	24.1
25	23.3	13.9	15.8	18.2	26.9	26.8
30	25.4	16.0	18.6	20.2	28.8	29.2
Surface	all extrudates were smooth and glossy up to 55 g/min.					

TABLE 4

	Control	Example 20	Control	Example 21
COMPOSITION (% by wt.)				
Hydrocarbon Polymer A	99.96	99.98	99.96	99.98
Fluorocarbon Polymer 2A	-	0.01	-	0.01
Fluorocarbon Polymer 1B	0.04	0.01	-	-
Fluorocarbon Polymer 1C	-	-	0.04	0.01
Throughput (g/min.)	Die Pressure (MPa)			
10	17.4	8.7	22.3	19.7
15	21.5	10.9	26.8	23.6
20	24.5	12.7	29.6	26.0
25	27.1	14.8	31.7	28.3
30	29.4	17.0	33.3	30.4
Surface	S,G below 38 g/min.	S,G below 55 g/min.	S,G below 28 g/min.	S,G to 55 g/min.

S - smooth
G - glossy
R - rough
D - dull

TABLE 5

Examples	22	23	24	25	26
COMPOSITION (% by wt.)					
Hydrocarbon Polymer A	99.98	99.98	99.98	99.98	99.98
Fluorocarbon Polymer 1A	0.01	0.01	0.01	0.01	0.01
Fluorocarbon Polymer 2B	0.01	-	-	-	-
Fluorocarbon Polymer 2C	-	0.01	-	-	-
Fluorocarbon Polymer 2D	-	-	0.01	-	-
Fluorocarbon Polymer 2E	-	-	-	0.01	-
Fluorocarbon Polymer 2F	-	-	-	-	0.01
Throughput (g/min.)	-------------------Die Pressure (MPa)---------------				
10	19.3	20.0	19.8	19.3	18.4
15	23.2	22.7	23.8	23.7	22.6
20	25.9	25.2	27.0	26.7	25.6
25	28.4	27.6	29.6	29.4	28.3
30	30.6	29.7	-	31.7	30.7
Surface	all surfaces smooth and glossy below 38 g/min.				

TABLE 6

	Control	Control	Example 27	Control	Control	Example 28
COMPOSITION (% by wt.)						
Hydrocarbon Polymer B	100	99.96	99.98	-	-	-
Hydrocarbon Polymer C	-	-	-	100	99.92	99.96
Fluorocarbon Polymer 1A	-	0.04	0.01	-	0.08	0.02
Fluorocarbon Polymer 2A	-	-	0.01	-	-	0.02
Throughput (g/min.)	---------------------------Die Pressure (MPa)---------------					
10	25.4	19.0	-	-	-	-
15	unstable	19.6	17.9	12.4	11.9	11.5
20	unstable	21.5	19.3	13.6	13.1	12.9
25	unstable	-	-	14.7	14.2	14.0
30	unstable	-	-	15.7	15.0	14.9
Surface	R,D above 10 g/min.	S,G to 23 g/min.	S,G to 23 g/min.	S,G to 38 g/min.	S,G to 38 g/min	S,G to* 38 g/min.

S - smooth
G - glossy
R - rough
D - dull

*These extrudates did not have the occasional cloudy streaks that appeared in the controls.

TABLE 7

	Control	Control	Example 29
COMPOSITION (% by wt.)			
Fluorocarbon Polymer 1A	-	0.02	0.02
Fluorocarbon Polymer 2A	-	-	0.02
Starting pressure, MPa	25.4	25.6	25.1
Starting throughput, g/min.	25.7	24.7	24.7
Ending pressure, MPa	25.4	24.8	19.7
Ending throughput, g/min.	25.7	24.9	25.8
Surface	rough	smooth glossy	smooth glossy

Claims

1. Composition comprising a difficultly-melt-processible polymer and 0.002-0.5 wt. % of a fluoropolymer process aid that:

(a) has a fluorine to carbon ratio of at least 1:1.5,

(b) has polymer chain ends bearing a functional group, W, wherein W is selected from -COF, $-SO_3M$, $-OSO_3M$ and -COOM, wherein M is hydrogen, a metal cation or a quaternary ammonium cation,

(c) is selected from the group consisting of

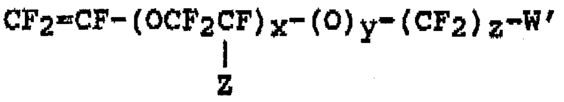
(i) an irradiated polytetrafluoroethylene,

(ii) a partially crystalline copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether) or a perfluoroolefin containing 3-8 carbon atoms,

(iii) an elastomeric copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether),

(iv) a copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, and

(v) a copolymer of tetrafluoroethylene and 0.5-40 mole % of a functional-group-containing monomer



$$CF_2{=}CF{-}(OCF_2\underset{\underset{Z}{|}}{CF})_x{-}(O)_y{-}(CF_2)_z{-}W'$$

wherein Z is -F or $-CF_3$, x is 0 or an integer of 1-4, y is 0 or 1, z is an integer of 1-12, and W' is selected from $-SO_2F$, $-SO_2Cl$, $-SO_3H$, -COOR or -COOM, wherein R is C_{1-3} alkyl and M is hydrogen, a metal cation, or a quaternary ammonium cation, and

(d) contains at least 100 functional groups W per million carbon atoms.

2. Composition of Claim 1 wherein the difficultly-melt-processible polymer is selected from mono-olefin polymers; vinyl aromatic polymers; copolymers of alpha-olefins and vinyl esters, (meth)acrylic esters, (meth)acrylic acids and their (ionomeric) metal salts or acrylonitrile; chlorinated polyethylene; polyvinyl chloride; polyamide; and polyester.

3. The composition of Claim 1 comprising a mixture of fluoropolymer process aids.

4. The composition of Claim 1 comprising a mixture of difficultly-melt-processible polymers.

5. The composition of Claim 1 wherein the difficultly-melt-processible polymer is a polymeric alloy.

6. Process comprising melt extruding a difficultly-melt-processible polymer having incorporated therein an effective amount, to improve processibility, of a fluoropolymer process aid that:

(a) has a fluorine to carbon ratio of at least 1:1.5,

(b) has polymer chain ends bearing a functional group, W, wherein W is selected from -COF, $-SO_3M$, $-OSO_3M$, and -COOM, wherein M is hydrogen, a metal cation or a quaternary ammonium cation,

(c) is selected from the group consisting of

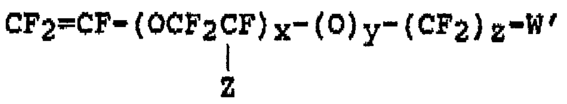
  (i) an irradiated polytetrafluoroethylene,

  (ii) a partially crystalline copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether) or a perfluoroolefin containing 3-8 carbon atoms,

  (iii) an elastomeric copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether),

(iv) a copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, and

(v) a copolymer of tetrafluoroethylene and 0.5-40 mole % of a functional-group-containing monomer



$$CF_2{=}CF{-}(OCF_2\underset{\displaystyle Z}{\underset{|}{C}}F)_x{-}(O)_y{-}(CF_2)_z{-}W'$$

wherein Z is -F or $-CF_3$, x is 0 or an integer of 1-4, y is 0 or 1, z is an integer of 1-12, and W' is selected from $-SO_2F$, $-SO_2Cl$, $-SO_3H$, -COOR or -COOM, wherein R is C_{1-3} alkyl and M is hydrogen, a metal cation, or a quaternary ammonium cation, and

(d) contains at least 100 functional groups W per million carbon atoms.

7. Process of Claim 6 wherein the concentration of fluoropolymer is 0.002-0.5 wt. %, based on the difficultly-melt-processible polymer.

8. Process of Claim 6 wherein the difficultly-melt-processible polymer has incorporated therein a mixture of fluoropolymer process aids.

9. Process of Claim 6 wherein the difficultly-melt-processible polymer is comprised of a mixture of such polymers.

10. Process of Claim 6 wherein the difficultly-melt-processible polymer is a polymeric alloy.

11. Polymer blend composition having improved processibility and comprising:

(a) a major portion of a difficultly melt-processible polymer, and

(b) a minor portion of:

(1) at least an effective amount, to improve processibility, of a fluorocarbon copolymer which at the melt-processing temperature of (a) is either in a melted form if crystalline, or is above its glass transition temperature if amorphous, and

(2) at least an effective amount, to improve processibility, of at least one tetrafluoroethylene homopolymer or copolymer of tetrafluoroethylene and at least one monomer copolymerizable therewith, wherein the mole ratio of fluorine to hydrogen is at least 1:1, and which is solid at the melt-processing temperature of (a).

12. Composition of Claim 11 wherein the difficultly-melt-processible polymer is selected from the group consisting of mono-olefin polymers; vinyl aromatic polymers; copolymers of alpha-olefins and vinyl esters, (meth)acrylic esters, acrylonitrile, or (meth)acrylic acids and their (ionomeric) metal salts; chlorinated polyethylene; polyvinyl chloride; polyester and polyamide.

13. Composition of Claim 11 wherein component (b)(1) is a fluorocarbon copolymer of vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene, tetrafluoroethylene, a perfluoro(alkyl vinyl ether),

1-hydropentafluoropropylene or 2-hydropentafluoropropylene.

14. Composition of Claim 13 wherein component (b)(1) is a copolymer of vinylidene fluoride and a monomer selected from hexafluoropropylene, chlorotrifluoroethylene, 1-hydropentafluoropropylene and 2-hydropentafluoropropylene; a copolymer of vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene or 1- or 2-hydropentafluoropropylene; a copolymer of tetrafluoroethylene and propylene; a copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether); or a copolymer of tetrafluoroethylene and hexafluoropropylene.

15. Composition of Claim 11 wherein component (b)(2) is a copolymer of tetrafluoroethylene and one or more monomers selected from ethylene, a perfluoroolefin, a perfluoro(alkyl vinyl ether) or a perfluoro(alkyl vinyl ether) containing a functional group.

16. Processing aid composition for a difficultly-melt-processible polymer, said composition consisting essentially of:

(a) a major portion of a polymer that is compatible with the difficultly-melt-processible polymer, and

(b) a minor portion of, with the parts totaling 100 parts:

(1) 2-95 parts by weight of a fluorocarbon copolymer which at the melt-processing temperature of the difficultly melt-processible polymer is either in a melted form if crystalline or is above its

glass transition temperature if amorphous; and

(2) 98-5 parts by weight of a tetrafluoroethylene homopolymer or copolymer of tetrafluoroethylene and a monomer which is copolymerizable therewith, wherein the mole ratio of fluorine to hydrogen is at least 1:1, and which is solid at the melt-processing temperature of the difficultly melt-processible polymer.

17. Composition of Claim 16 wherein component (b)(1) is a fluorocarbon copolymer of vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene, tetrafluoroethylene, a perfluoro(alkyl vinyl ether), 1-hydropentafluoropropylene or 2-hydropentafluoropropylene.

18. Composition of Claim 17 wherein component (b)(1) is a copolymer of vinylidene fluoride and a monomer selected from hexafluoropropylene, chlorotrifluoroethylene, 1-hydropentafluoropropylene and 2-hydropentafluoropropylene; a copolymer of vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene or 1- or 2-hydropentafluoropropylene; a copolymer of tetrafluoroethylene and propylene; a copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether); or a copolymer of tetrafluoroethylene and hexafluoropropylene.

19. Composition of Claim 16 wherein component (b)(2) is a copolymer of tetrafluoroethylene and one or more monomers selected from ethylene, a

perfluoroolefin, a perfluoro(alkyl vinyl ether) or a perfluoro(alkyl vinyl ether) containing a functional group.

20. Composition of Claim 16 wherein the compatible polymer is a difficultly melt-processible polymer.

21. Composition of Claim 16 wherein the difficultly-melt-processible polymer is selected from the group consisting of mono-olefin polymers; vinyl aromatic polymers; copolymers of alpha-olefins and vinyl esters, (meth)acrylic esters, acrylonitrile, or (meth)acrylic acids and their (ionomeric) metal salts; chlorinated polyethylene; polyvinyl chloride; polyester and polyamide.

22. Extrusion process comprising melt extruding a difficultly melt-processible polymer having incorporated therein an effective amount, to improve processibility, of a processing aid consisting essentially of, with the parts totaling 100 parts:

(a) 2-95 parts by weight of a fluorocarbon copolymer which at the melt-processing temperature of the difficultly melt-processible polymer is either in a melted form if crystalline or is above its glass transition temperature if amorphous; and

(b) 98-5 parts by weight of a tetrafluoroethylene homopolymer or copolymer of tetrafluoroethylene and a monomer which is copolymerizable therewith, wherein the mole ratio of fluorine to hydrogen is at least 1:1, and which is solid at the melt-processing temperature of the difficultly melt-processible polymer.

23. Process of Claim 22 wherein the difficultly-melt-processible polymer is selected from the group consisting of mono-olefin polymers; vinyl aromatic polymers; copolymers of alpha-olefins and vinyl esters, (meth)acrylic esters, acrylonitrile, or (meth)acrylic acids and their (ionomeric) metal salts; chlorinated polyethylene; polyvinyl chloride; polyester; and polyamide

24. Process of Claim 22 wherein component (a) is a fluorocarbon copolymer of vinylidene fluoride, hexafluoropropylene, chlorotrifluoroethylene, tetrafluoroethylene, a perfluoro(alkyl vinyl ether), 1-hydropentafluoropropylene or 2-hydropentafluoropropylene.

25. Process of Claim 24 wherein component (a) is a copolymer of vinylidene fluoride and a monomer selected from hexafluoropropylene, chlorotrifluoroethylene, 1-hydropentafluoropropylene and 2-hydropentafluoropropylene; a copolymer of vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene or 1- or 2-hydropentafluoropropylene; a copolymer of tetrafluoroethylene and propylene; a copolymer of tetrafluoroethylene and a perfluoro(alkyl vinyl ether); or a copolymer of tetrafluoroethylene and hexafluoropropylene.

26. Process of Claim 22 wherein component (b) is a copolymer of tetrafluoroethylene and one or more monomers selected from ethylene, a perfluoroolefin, a perfluoro(alkyl vinyl ether) or a perfluoro(alkyl vinyl ether) containing a functional group.

FIGURE 1

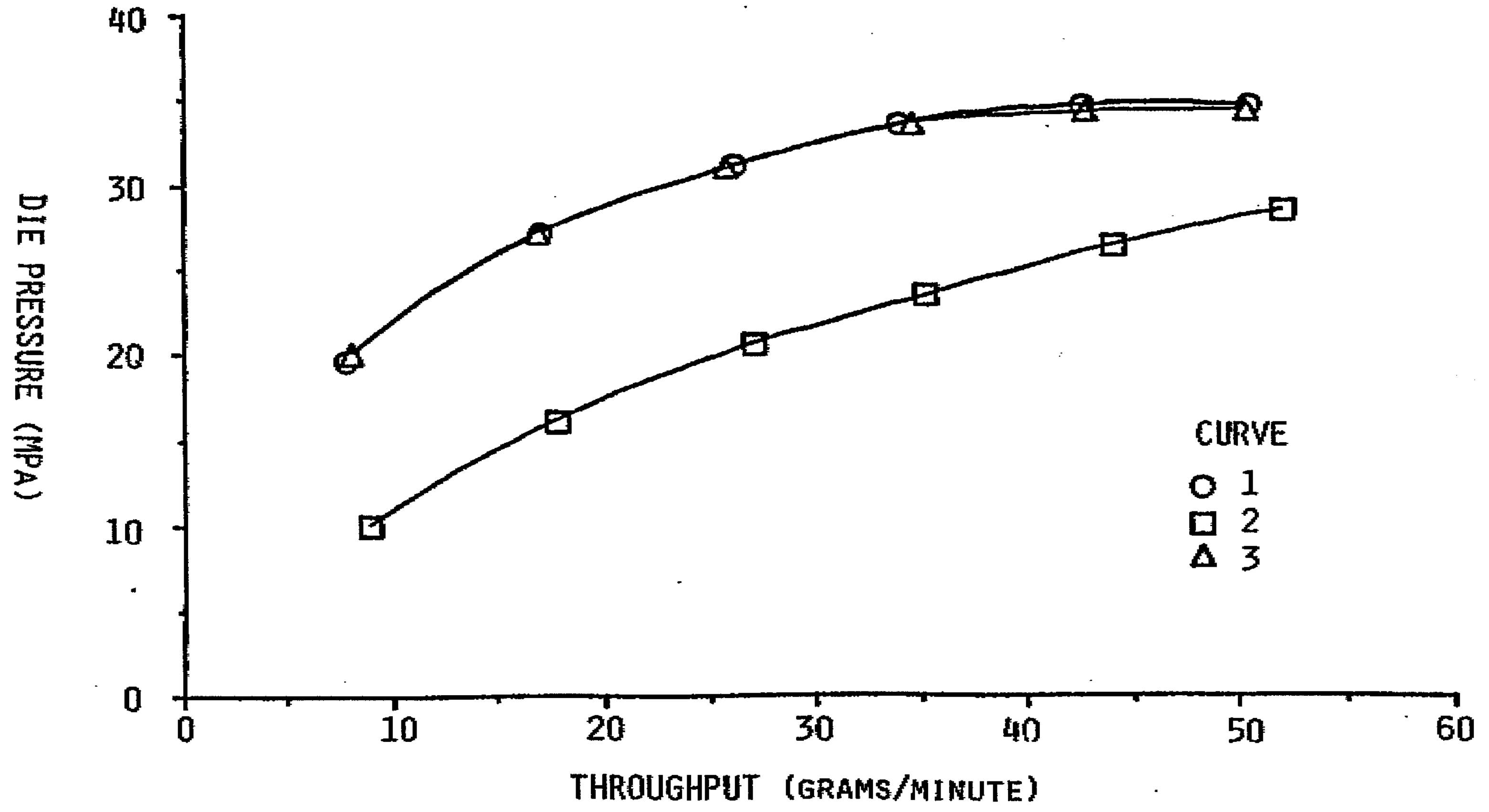

40
30
20
10
0
DIE PRESSURE (MPA)
0
10
20
30
40
50
60
THROUGHPUT (GRAMS/MINUTE)
CURVE
○ 1
□ 2
△ 3

FIGURE 2

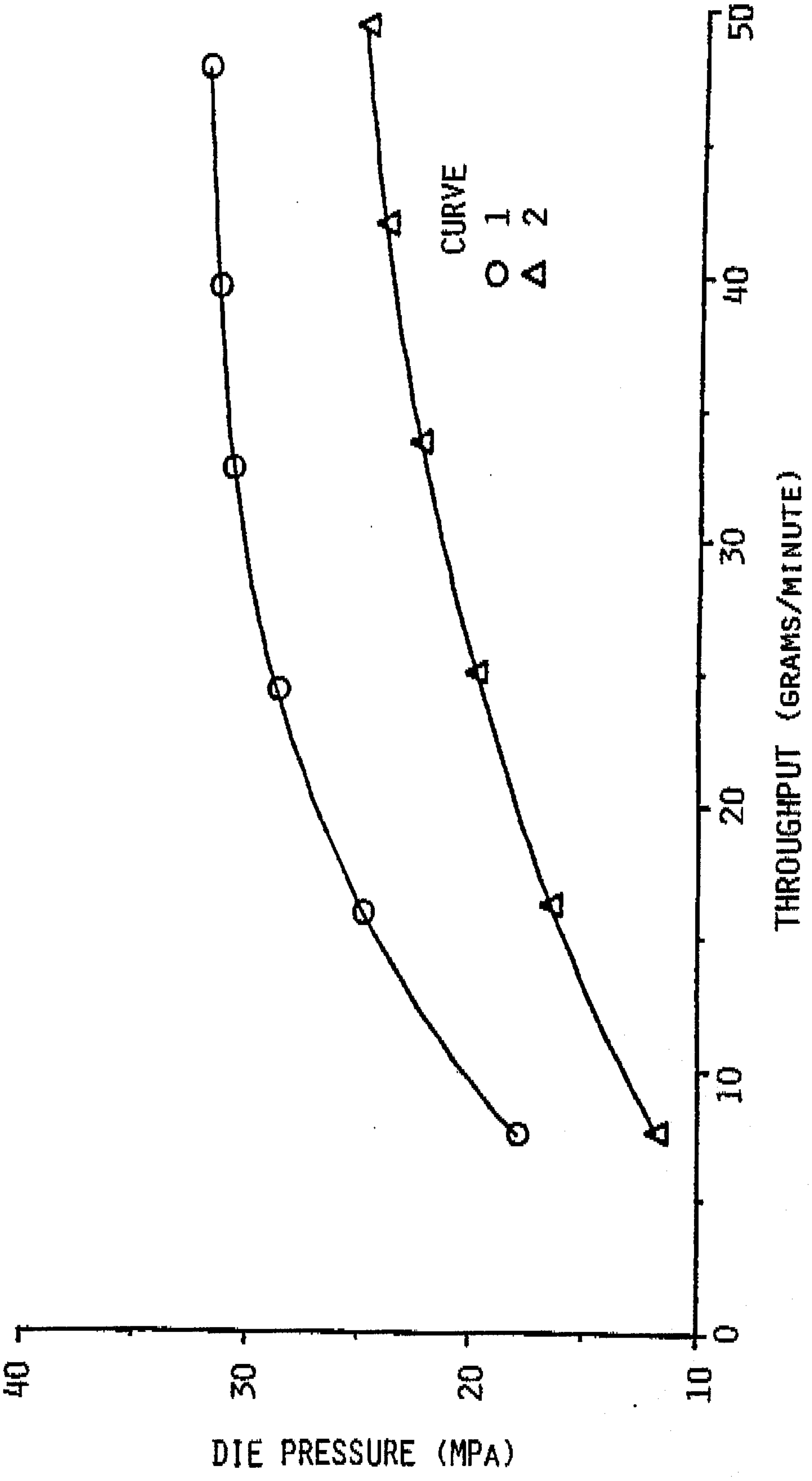

CURVE
○ 1
△ 2
DIE PRESSURE (MPA)
10
20
30
40
THROUGHPUT (GRAMS/MINUTE)
0
10
20
30
40
50

FIGURE 3

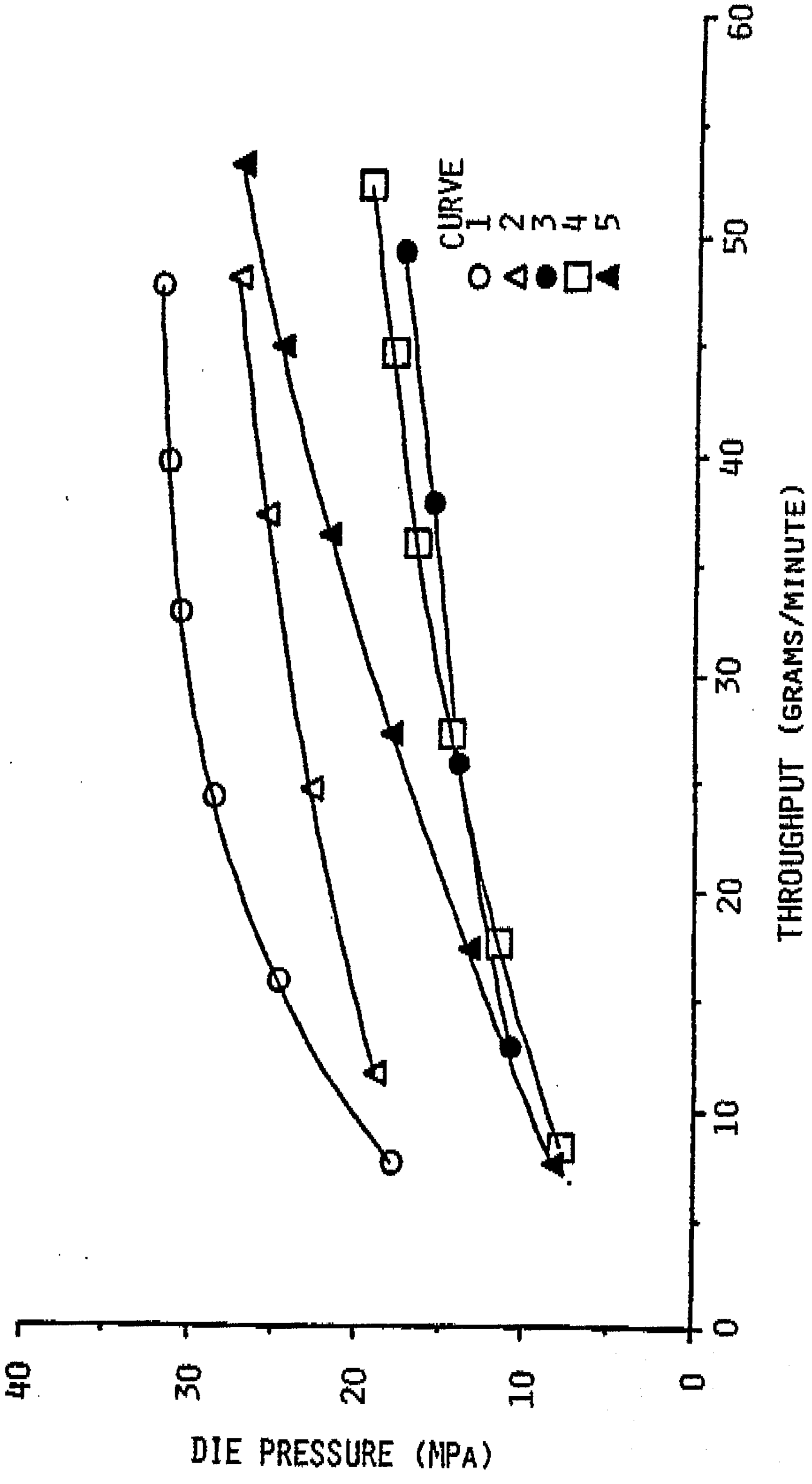
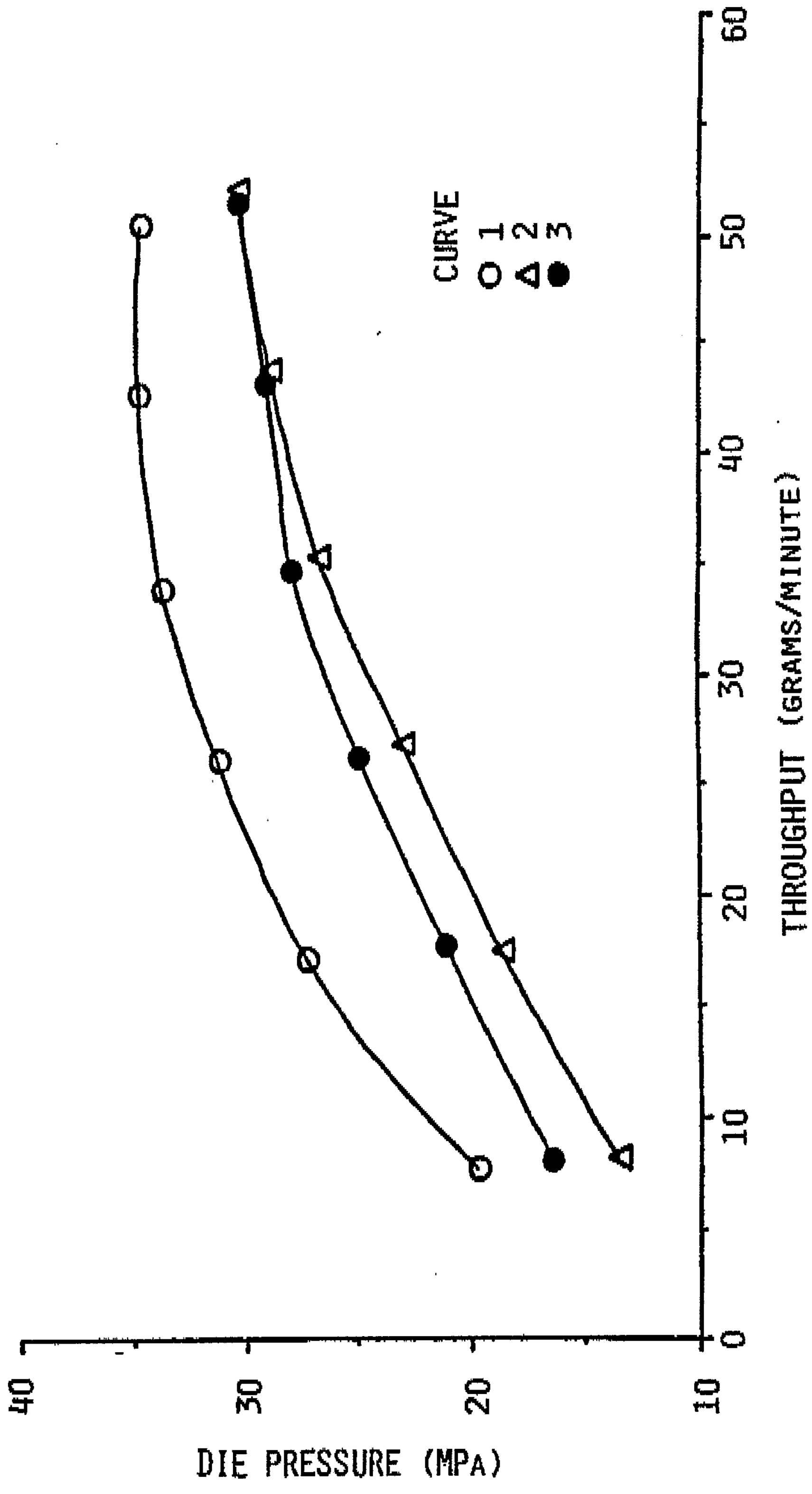

DIE PRESSURE (MPA)
0
10
20
30
40
THROUGHPUT (GRAMS/MINUTE)
0
10
20
30
40
50
60
CURVE
○ 1
△ 2
● 3
□ 4
▲ 5

FIGURE 4


CURVE
○ 1
△ 2
● 3
DIE PRESSURE (MPa)
40
30
20
10
THROUGHPUT (GRAMS/MINUTE)
0
10
20
30
40
50
60

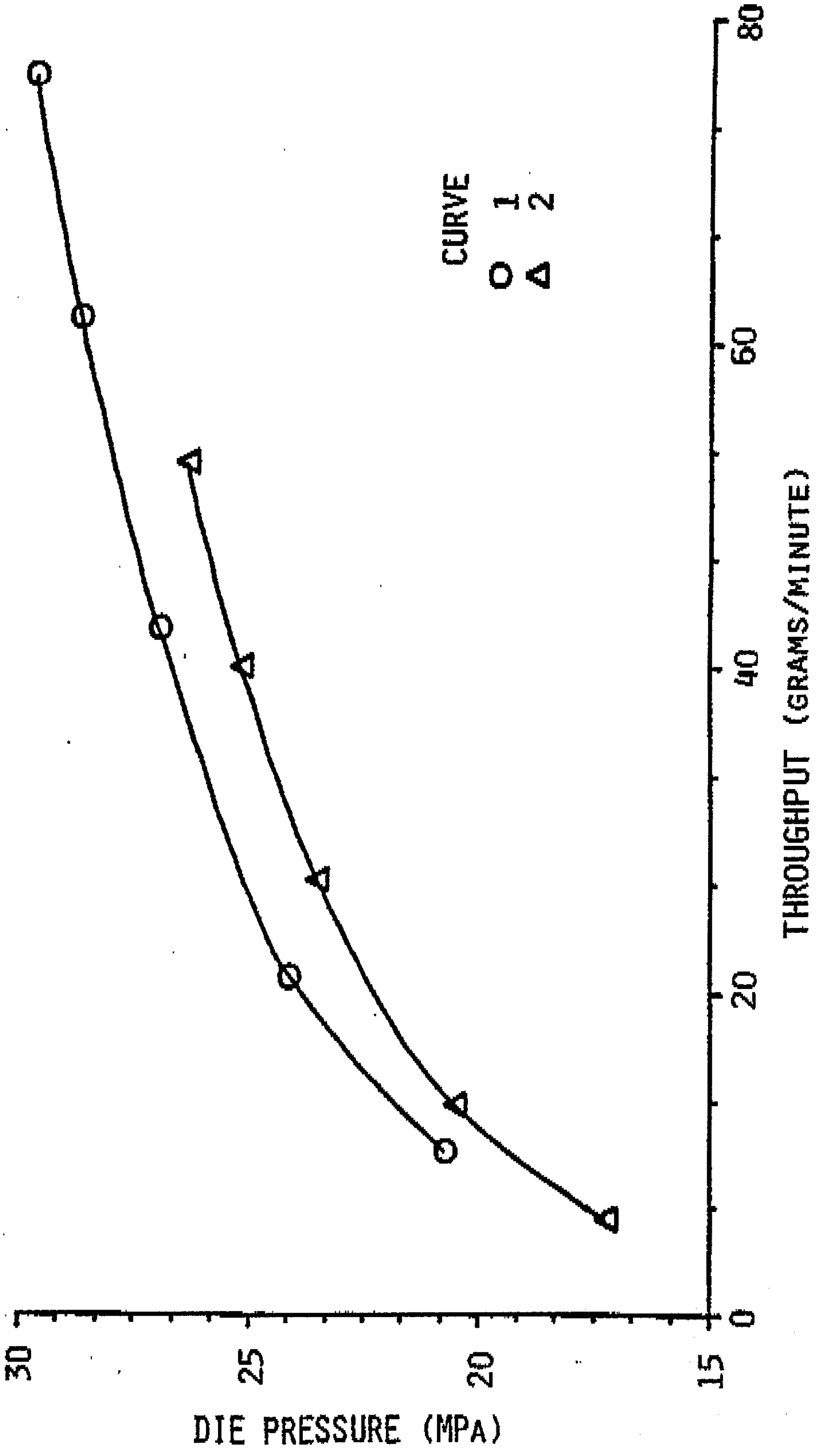

CURVE
○ 1
△ 2
THROUGHPUT (GRAMS/MINUTE)
0
20
40
60
80
DIE PRESSURE (MPA)
15
20
25
30

FIGURE 5

FIGURE 6

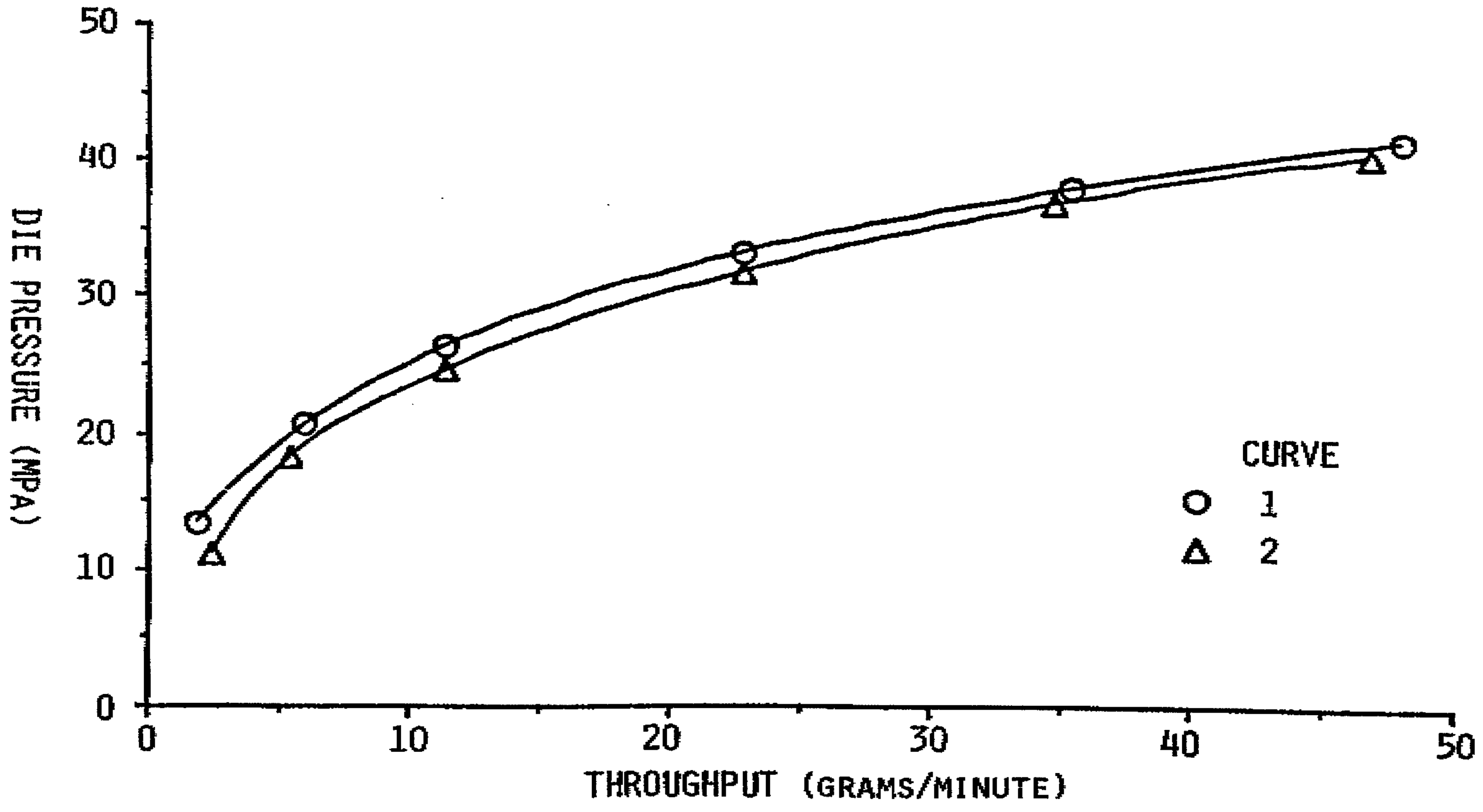

50
40
30
20
10
0
DIE PRESSURE (MPA)
0
10
20
30
40
50
THROUGHPUT (GRAMS/MINUTE)
CURVE
○ 1
△ 2

FIGURE 7

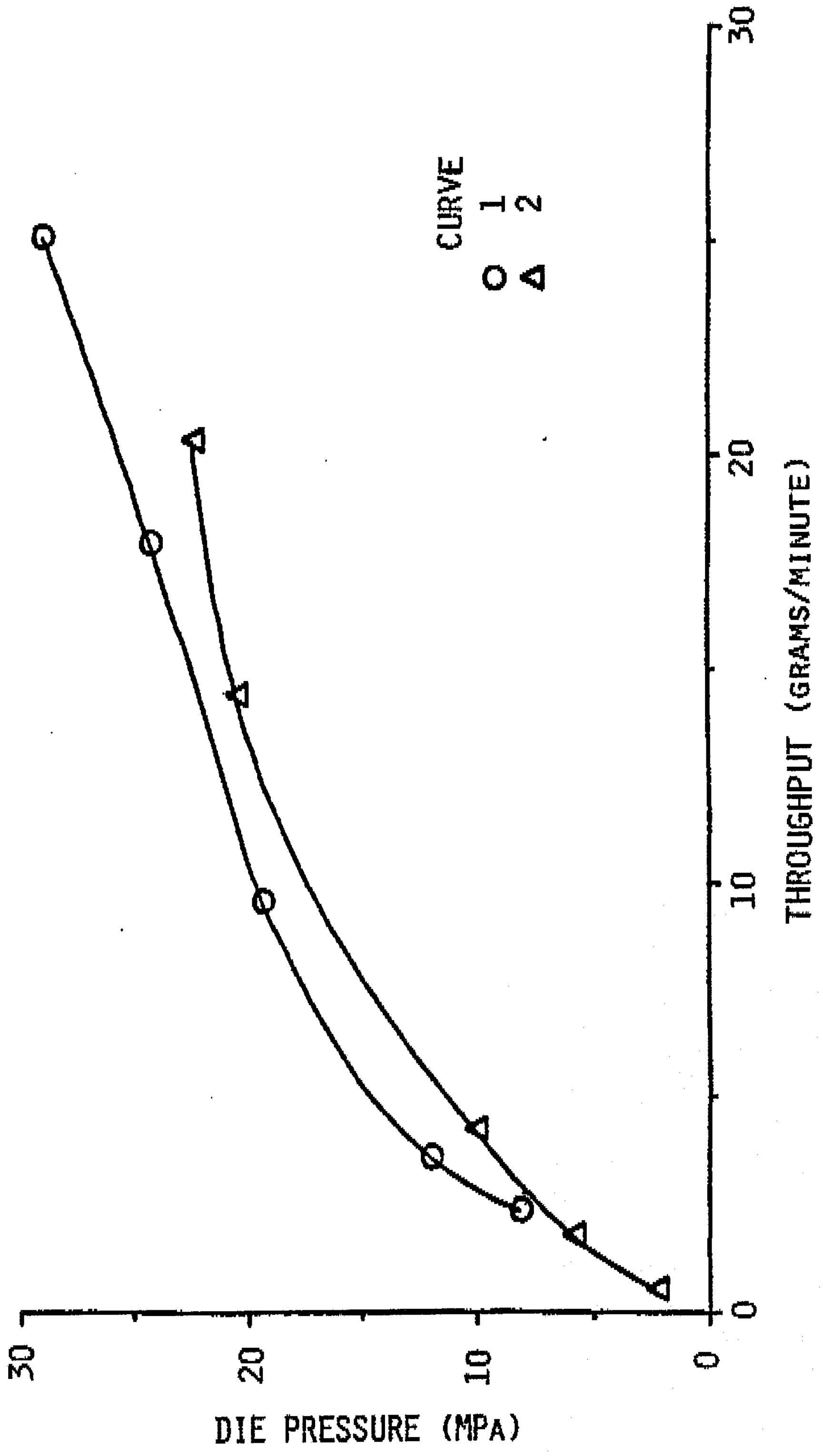

CURVE
○ 1
△ 2
DIE PRESSURE (MPA)
0
10
20
30
THROUGHPUT (GRAMS/MINUTE)
0
10
20
30

FIGURE 8

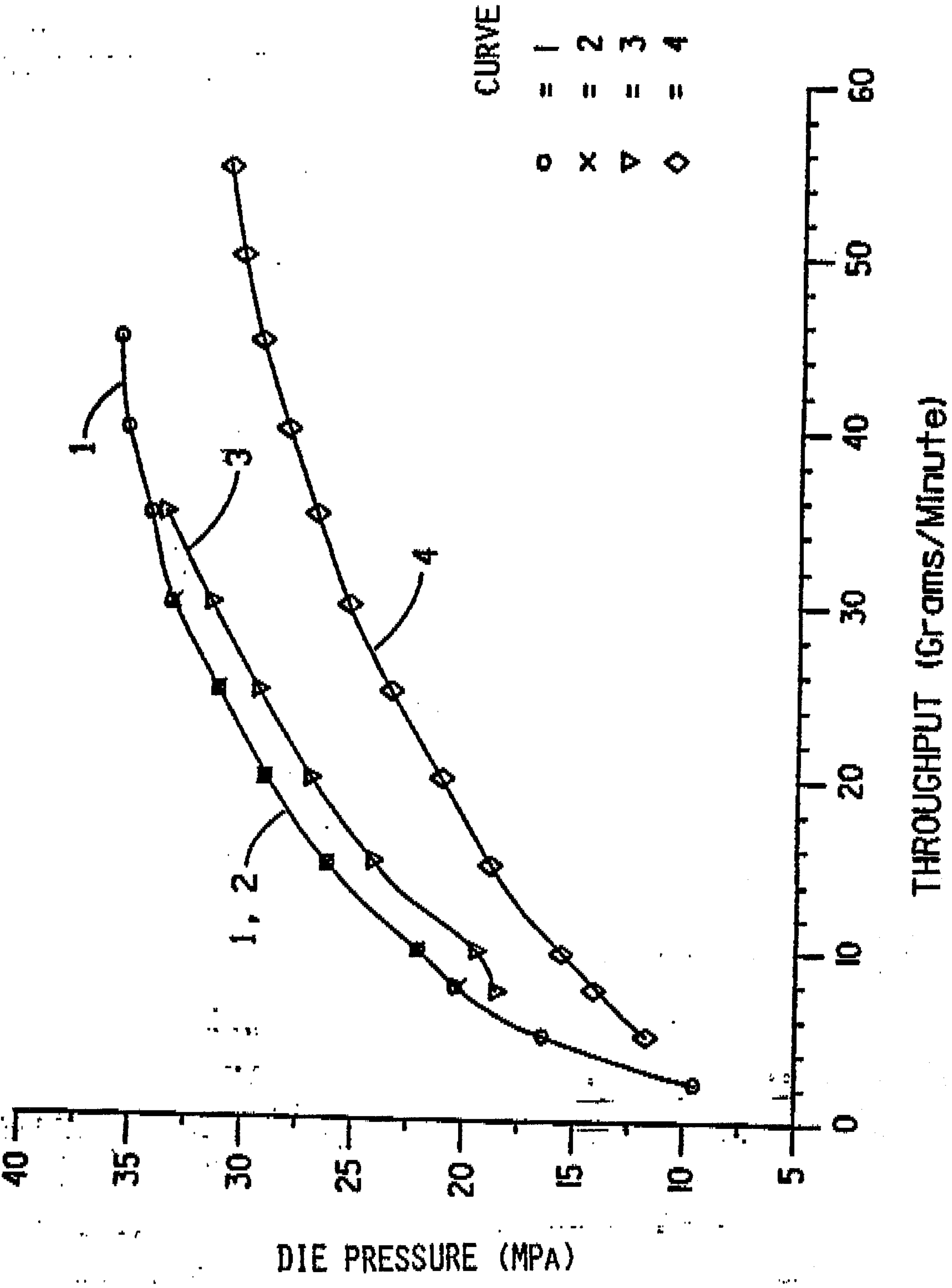
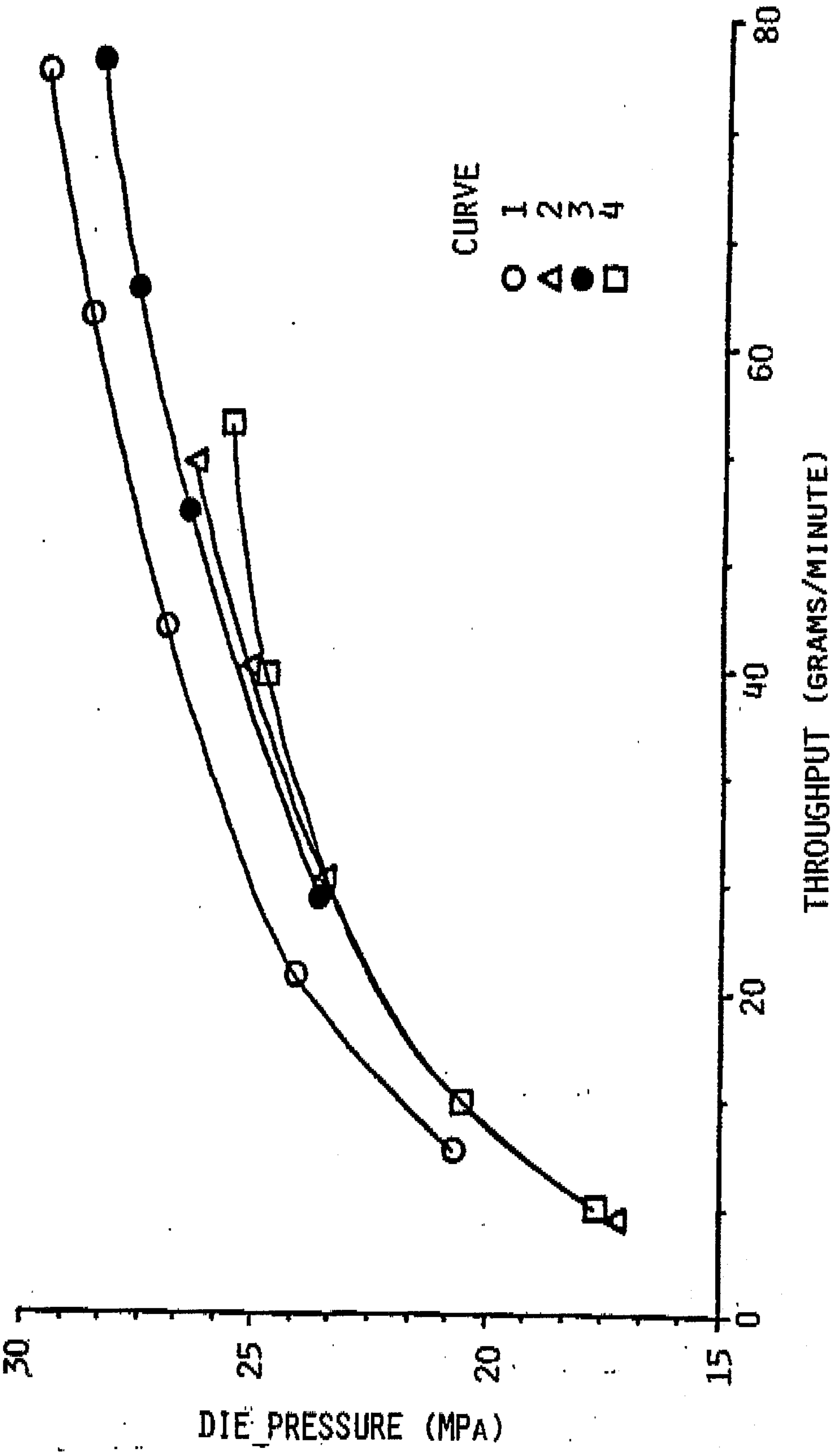

CURVE
o = 1
x = 2
▽ = 3
◇ = 4
1
3
4
1, 2
DIE PRESSURE (MPA)
40
35
30
25
20
15
10
5
THROUGHPUT (Grams/Minute)
0
10
20
30
40
50
60

FIGURE 9



SUBSTITUTE SHEET

FIGURE 10

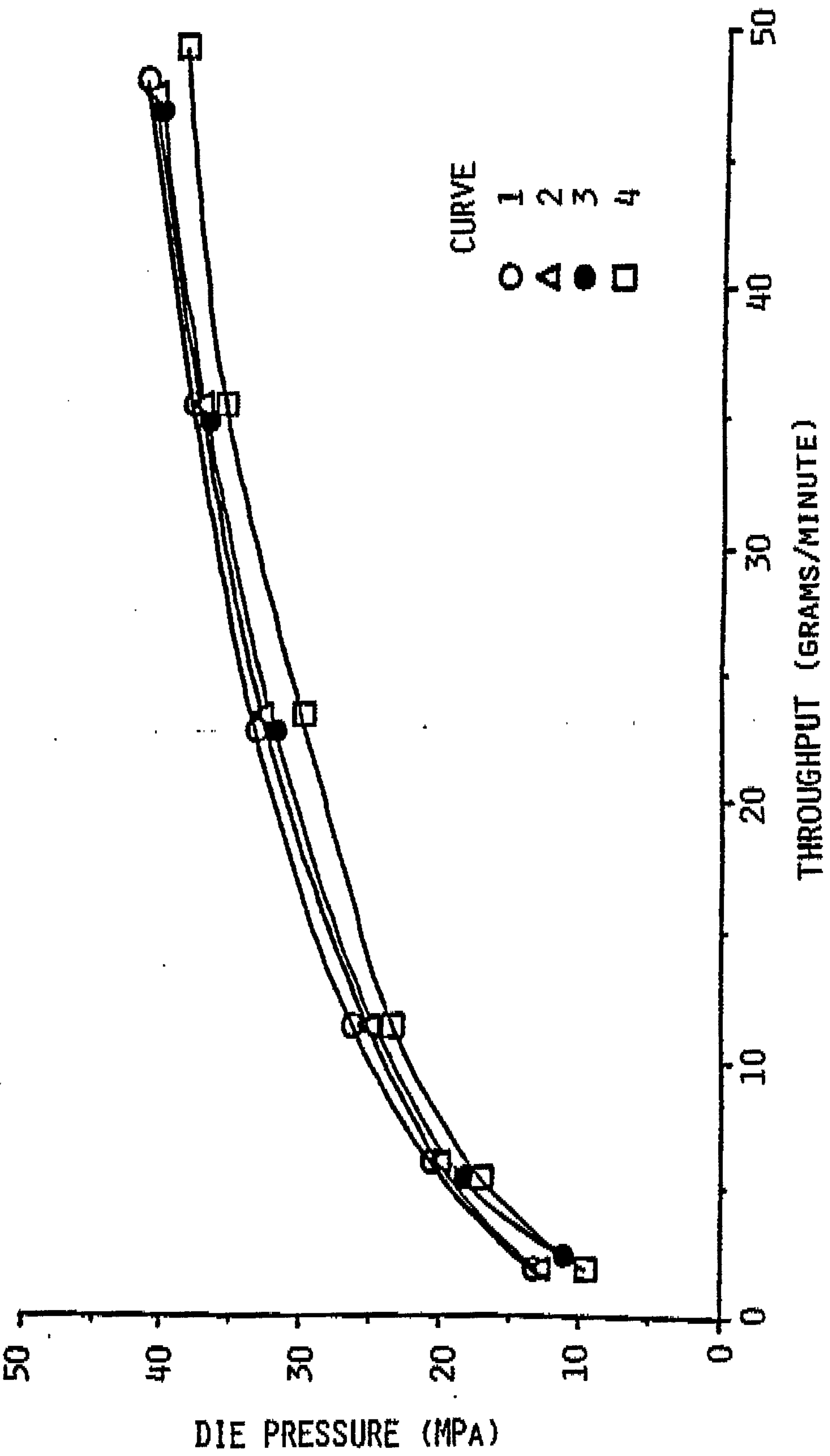
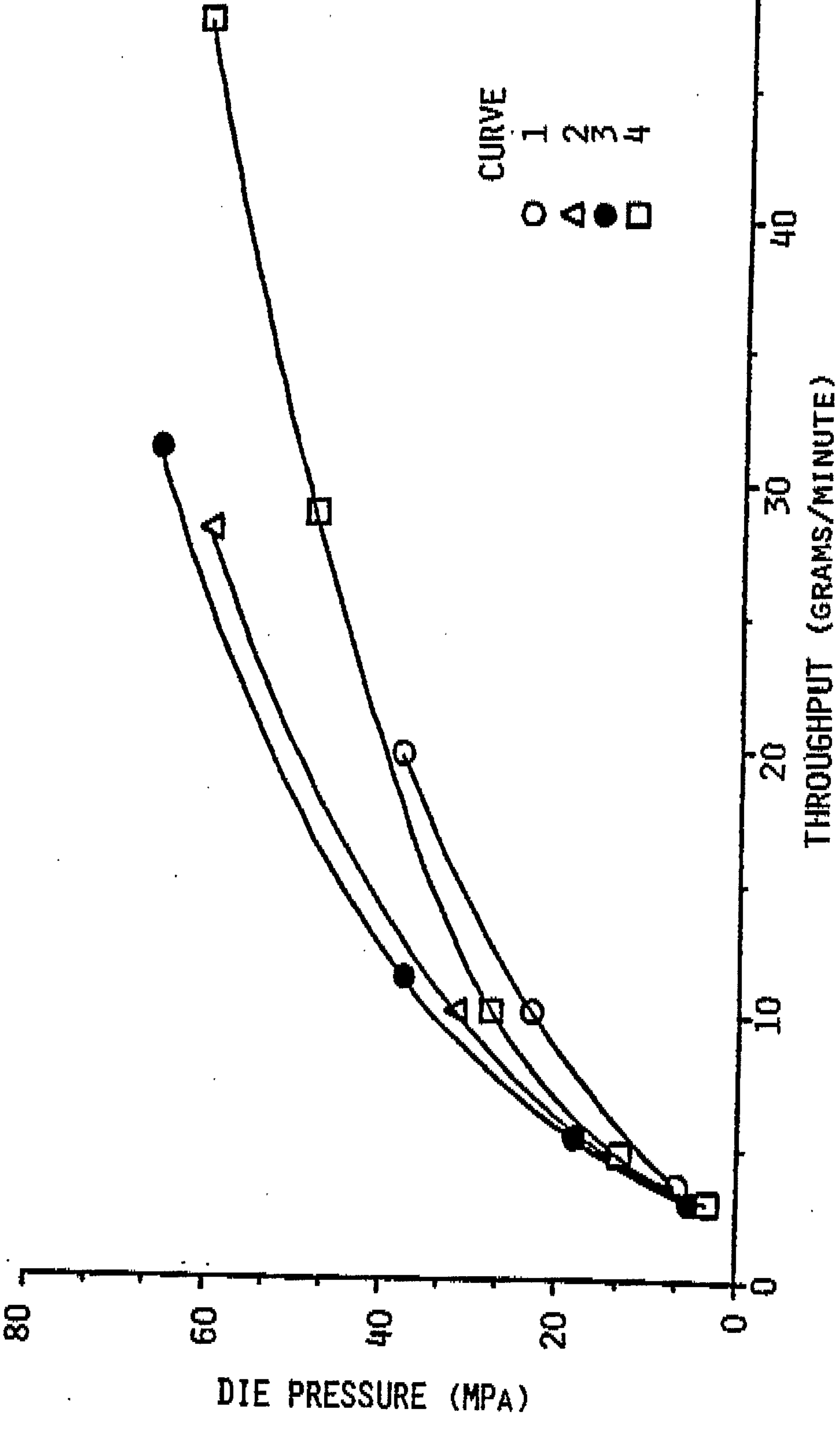

CURVE
○ 1
△ 2
● 3
□ 4
DIE PRESSURE (MPa)
0
10
20
30
40
50
THROUGHPUT (GRAMS/MINUTE)
0
10
20
30
40
50

FIGURE 11


CURVE
○ 1
△ 2
● 3
□ 4
THROUGHPUT (GRAMS/MINUTE)
0
10
20
30
40
50
DIE PRESSURE (MPA)
0
20
40
60
80

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/05557

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 L 101/00, C 08 L 23/02,//(C 08 L 101/00, 27:12), (C 08 L 23/02, 27:12)

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 L, C 08 F, C 09 D, C 08 J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[*]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	US, A, 3147314 (E.F. CUFF) 1 September 1964 see column 3, lines 51-61; claims --	1-10
Y	US, A, 4863983 (JOHNSON et al.) 5 September 1989 see column 3, line 57 - colum 4, line 22; claims --	1-10
A	EP, A, 0282882 (HOECHST) 21 September 1988 --	
A	EP, A, 0169069 (BP CHEMICALS) 1 January 1986 --	
A	EP, A, 0088414 (DAIKIN KOGYO) 14 September 1983 --	

./.

- [*] Special categories of cited documents:[10]
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 25th January 1991	Date of Mailing of this International Search Report 04.03.91
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Alfredo Prein

Form PCT/ISA/210 (second sheet) (January 1985)

International Application No PCT/US 90/05557 -2-

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	Patent Abstracts of Japan, vol. 8, no. 232 (C-248)(1669), 25 October 1984, & JP, A, 59113059 (MITSUI SEKIYU KAGAKU KOGYO K.K.) 29 June 1984 cited in the application --	
P,X	US, A, 4904735 (CHAPMAN Jr. et al.) 27 February 1990 see the whole document cited in the application --	11-26
A	Research Disclosure, August 1989, "Hexafluoropropene/vinylidene fluoride copolymer processing aid for ionomers of ethylene/methacrylic acid copolymers", see page 569, abstract 30417 -----------	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9005557 SA 41160

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 19/02/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3147314		None	
US-A- 4863983	05-09-89	AU-A- 3271789	19-10-89
		JP-A- 2043267	13-02-90
		US-A- 4983677	08-01-91
EP-A- 0282882	21-09-88	DE-A- 3708384	22-09-88
		AU-B- 597158	24-05-90
		AU-A- 1303688	15-09-88
		JP-A- 63245450	12-10-88
		US-A- 4829116	09-05-89
		ZA-A- 8801755	31-08-88
EP-A- 0169069	22-01-86	AU-B- 578960	10-11-88
		AU-A- 4510785	23-01-86
		CA-A- 1257435	11-07-89
		JP-A- 61106667	24-05-86
		US-A- 4707517	17-11-87
EP-A- 0088414	14-09-83	JP-A,B 58174407	13-10-83
		US-A- 4552925	12-11-85
US-A- 4904735	27-02-90	None	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82