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(54) Title: PLASTICIZED FLUOROPOLYMERS (57) Abstract Fluoroelastomers and fluoroplastics are plasticized with high-boiling fluorinated aliphatic cyclic structures to enhance processibility or to improve final properties.		

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TITLE

PLASTICIZED FLUOROPOLYMERS

FIELD OF THE INVENTION

This invention is in the field of plasticized fluoropolymers,
5 including both fluoroplastics and fluoroelastomers.

BACKGROUND OF THE INVENTION

Plasticizing additives are used in plastics and elastomers to
achieve various effects. Such plasticizers may improve melt processing
characteristics or may modify physical properties of the polymer under use
10 conditions, or both.

Highly fluorinated polymers have desirable combinations of
electrical, chemical, and thermal properties. However, the high molecular
weight required to realize the properties necessary for severe service conditions
can make fluoropolymers difficult to process. Tetrafluoroethylene (TFE)
15 homopolymers are so intractable that conventional melt processing techniques
cannot be used and articles are fabricated by methods adapted from powder
metallurgy. Partially-crystalline copolymers of TFE with other fluorinated
monomers are melt-fabricable but processing rates are limited, especially for
grades designated for the most severe service. Likewise, the rates at which
20 fluoroelastomers, both vinylidene fluoride (VF₂) copolymers and
perfluoroelastomers, can be shaped are limited. In addition, the accessible
balance of properties for fluoroelastomers is unsatisfactory for some uses, a
softer or less stiff compound frequently being desired.

U.S. Patent 3,665,067 discloses the use of hexafluorobenzene as
25 a plasticizer for polytetrafluoroethylene (PTFE) in the fabrication process
known as ram extrusion. U.S. Patent 4,012,453 discloses the use of
chlorofluorinated aromatic hydrocarbons as plasticizers for
trifluorochloroethylene polymers.

U.S. Patent 2,510,078 discloses the use of fluorinated oils as
30 plasticizers for certain fluoroplastics including PTFE. U.S. Patent 3,434,996
discloses the use of chlorofluorinated ethanes as extrusion lubricants for PTFE
to overcome the deleterious effect on properties of oils, greases, and waxes
when used as plasticizers. U.S. Patent 3,030,328 discloses a copolymer of TFE
and a fluorinated alpha-olefin plasticized with esters of fluoroalcohols with
35 cyclic polycarboxylic acids to improve melt flow and toughness.

U.S. Patent 3,069,401 discloses the use of VF₂/HFP copolymer greases in VF₂/HFP fluoroelastomers to change viscosity without altering the properties of the cured elastomer. Since the chemical compositions of the grease and the fluoroelastomer are similar, this appears to be equivalent to
5 modifying the molecular weight distribution of the fluoroelastomer. U.S. Patent 4,810,765 teaches the use of cotelomers of VF₂ which can participate in peroxide curing of fluoroelastomers. U.S. Patent 3,804,801 discloses the use of a modified fluorosilicone polymer in a fluoroelastomer to improve low-temperature properties.

10 It is also known to use fluorinated polyethers as plasticizers for hydrogen-containing fluoroelastomers and perfluoroelastomers, as taught in by U.S. Patents 4,413,094; 4,894,418; and 5,061,759. However, the polyethers have limited compatibility with the fluoropolymers and will exude at moderate concentrations unless modified to participate in the curing reaction.

15 SUMMARY OF THE INVENTION

This invention provides fluoropolymers plasticized with high-boiling, highly-fluorinated, polycyclic alkane. In one embodiment, the plasticizer is an oligomer of predominantly perfluorinated aliphatic fused-ring structures, which oligomer is a very viscous liquid containing high-boiling
20 fractions that are glasses at room temperature.

Plasticized fluoroelastomers have enhanced processibility and an improved balance of properties. Plasticized fluoroplastics have enhanced processibility without sacrifice of properties.

BRIEF DESCRIPTION OF THE FIGURES

25 Fig. 1 compares the infrared spectra of C₁₄F₂₄ and oligomeric plasticizer of this invention.

Fig. 2 shows an oligomer of the phenanthrene structure.

Fig. 3 shows a dimer with alkyl fragments and unsaturation.

30 Fig. 4 is a graph showing viscosity vs. shear stress for plasticized TFE/HFP copolymer and control.

DETAILED DESCRIPTION OF THE INVENTION

The plasticizer of this invention is high-boiling, highly-fluorinated, polycyclic alkane. By high boiling is meant a boiling point
35 of at least about 280°C at atmospheric pressure. The boiling point may be the

lower end of a boiling range. "Highly-fluorinated" as used herein means that the ratio F/H is at least 100.

The plasticizer of this invention includes complex mixture of highly-fluorinated aliphatic cyclic structures, herein called "fluoroalicyclic oligomer" or sometimes just "oligomer", that can be obtained as high-boiling byproduct of the fluorination of compounds having cyclic, preferably polycyclic, carbon skeletons using CoF_3 and fluorine according to British Patent 1,281,822. The structures can have perfluoroalkyl side chains. When the crude product is refined by fractional distillation, the high-boiling byproduct fraction is obtained. This higher boiling fraction, designated "fluoroalicyclic oligomer" or "oligomer", has been found to be useful as a plasticizer in fluoropolymers. The fluoroalicyclic oligomer can be further refined or fractionated if desired.

A preferred fluoroalicyclic oligomer is the high-boiling byproduct of the fluorination of phenanthrene to produce perfluorotetradecahydrophenanthrene, $\text{C}_{14}\text{F}_{24}$ (Rhone-Poulenc Chemicals, ISC Division, UK). When phenanthrene is thus fluorinated, the high-boiling fraction (oligomer) obtained upon fractional distillation of the crude liquid product has a boiling range of about 280°-400°C at atmospheric pressure. As synthesized, oligomer is reported to contain small amounts of hydrogen and olefinic carbon. Post-treatment with fluorine to further fluorinate the highly-fluorinated oligomer is believed to reduce significantly, but not eliminate, the unsaturation and hydrogen content. The fluoroalicyclic oligomer derived from the fluorination of phenanthrene is herein designated "phen-oligomer" to indicate its source.

A fluorine-treated sample of phen-oligomer characterized in some detail was a viscous, transparent, colorless substance that boiled at about 322°C. Room-temperature viscosity is usually so high that the substance will not pour, remaining essentially undeformed when the container is tilted for several minutes. The material flows easily at about 60°C. Higher-boiling fractions are more viscous, and the highest-boiling fractions are glasses at room temperature, but flow readily at about 100°C.

A variety of analytical techniques led to the following characterization of this phen-oligomer fluoroalicyclic oligomer. As the wide boiling range would suggest, the material is a mixture of many components. ESCA and NMR indicated that the material is made up almost entirely of carbon and fluorine. Elemental analysis indicated hydrogen presence at 0.25 atomic

percent, but proton NMR revealed only a much smaller trace and the 2900 cm^{-1} region of the infrared spectrum (Fig. 1) shows no clearly discernible hydrogen. ^{19}F NMR indicated that six-membered-ring aliphatic structures predominate. Phenanthrene-like structures are believed to predominate, consistent with Fig. 1, but there is evidence that anthracene-like structures are also present. The generalized chemical formula might be $\text{C}_{14}\text{F}_{23}(\text{C}_{14}\text{F}_{22})_n\text{C}_{14}\text{F}_{23}$ with $n = 0-2$ predominating, as shown in Fig. 2. A wide diversity of structures would be obtained either by loss of fluorine atom pairs to create unsaturated carbon-carbon bonds or further ring closure, or by ring opening to yield perfluoroalkyl side groups. ESCA and NMR suggest that olefinic carbon may be present to the extent of 8% of total carbon. Fig. 3 shows a possible structure for an unsaturated dimer containing alkyl fragments.

The fluoropolymers of this invention are polymers of at least one fluorinated monomer, but may incorporate monomers containing no fluorine. The fluorinated monomers are selected from the group consisting of fluoroolefins and fluorinated vinyl ethers of the formula $\text{CY}_2=\text{CYOR}$ or $\text{CY}_2=\text{CYOR}'\text{OR}$ where Y is H or F, and -R, and -R' are independently completely-fluorinated or partially-fluorinated alkyl and alkylene groups containing 1-8 carbon atoms. Preferred -R groups contain 1-4 carbon atoms and are preferably perfluorinated. Preferred -R' groups contain 2-4 carbon atoms and are preferably perfluorinated. These fluoropolymers include hydrogen-containing fluoroelastomers, perfluoroelastomers, and fluoroplastics. Fluoroelastomers are distinguished from fluoroplastics by the general absence of crystallinity from fluoroelastomers, as evidenced by differential scanning calorimetry (DSC).

A wide variety of hydrogen-containing fluoroelastomers can be used in this invention. These polymers commonly, but not universally, incorporate vinylidene fluoride (VF_2) as a monomer. The most common fluoroelastomers are copolymers of VF_2 with hexafluoropropylene (HFP) and optionally TFE. Fluoroelastomers may include cure site moieties derived from chain transfer agents or small concentrations of cure site monomers, or both, usually to achieve peroxide-curable systems. Representative fluoroelastomers of this invention include those described in Rexford, U.S. Patent 3,057,677; Honn, et al, U.S. Patent 3,318,854; Pailthorp et al, U.S. Patent 2,968,649; Gladding et al, U.S. Patent 3,707,529; Tatamoto et al, U.S. Patent 4,243,770;

Apotheker et al, U.S. Patent 4,035,565 and Moore, U.S. Patent 4,973,633, all of which are hereby incorporated by reference. Perfluoroelastomers of this invention include those prepared from TFE, one or more perfluoro(alkyl vinyl) ethers (PAVE), and at least one cure site moiety. For purposes of the invention, 5 minor portions of the TFE can be replaced by other perhaloolefins, such as chlorotrifluoroethylene. Perfluoro(alkyl vinyl) ethers preferred for use in this invention include perfluoro(methyl vinyl) ether (PMVE) and perfluoro(propyl vinyl) ether (PPVE). Small concentrations of monomers which are not perfluorinated can also be used without significantly changing the desirable 10 characteristics of the perfluoroelastomers. Normally, such monomers are incorporated as cure sites to obtain desirable crosslinking characteristics and may be present in concentrations up to about 3 mol%. Such monomers can include, for example, bromotetrafluorobutene, bromotrifluoroethylene, and monomers containing cyano groups. Alternatively or additionally, chain 15 transfer agents which are not perfluorinated can be used in the polymerization reaction to introduce desirable fragments into the polymer for curing purposes, and are considered cure site moieties in the context of the present invention. Such agents include di-iodo compounds that result in bound iodine in the polymer, commonly at the end of the molecule. Representative 20 perfluoroelastomers are illustrated in U.S. Patents 3,467,638; 4,035,565; 4,281,092; 4,487,903; 4,529,784; 4,948,853 and 4,983,697; each of which is hereby incorporated by reference.

Fluoroplastics of this invention include but are not limited to the group known as TFE polymers. This group includes polytetrafluoroethylene 25 (PTFE), and copolymers of TFE with such small concentrations of copolymerizable modifying monomers that the resins remain non-melt-fabricable (modified PTFE). The modifying monomer can be, for example, HFP, PPVE, perfluorobutyl ethylene (PFBE), chlorotrifluoroethylene (CTFE), or other monomer that introduces side groups into the molecule. The 30 concentration of such modifiers is usually less than 1 mol%. The PTFE resins of this invention include both those derived from suspension polymerization (granular resin) and from emulsion polymerization (fine powder or coagulated dispersion resin). The group of TFE polymers also includes melt-fabricable copolymers of TFE with sufficient concentrations of one or more 35 copolymerizable monomer to reduce the melting point significantly below that

of PTFE. Such copolymers generally have melt viscosity in the range 0.5×10^3 to 60×10^3 Pa-s, but viscosities outside this range are known. Comonomers with TFE can include perfluoroolefins, PAVE, and ethylene (E), for example, and these are preferred. When the preferred comonomer is E, minor amounts of
5 a third monomer are used with PFBE or PPVE being especially preferred. Among perfluorinated comonomers, HFP and PPVE are most preferred. Other fluoroplastics within the scope of the invention are CTFE polymers including E/CTFE copolymers and vinylidene fluoride (VF_2) polymers including homopolymers and VF_2 copolymers with perfluoroolefins.

10 The concentration of high-boiling, highly-fluorinated, polycyclic alkane, e.g., fluoroalicyclic oligomer or phen-oligomer, used as plasticizer in the plasticized fluoropolymers of this invention varies with the fluoropolymer and the desired effect. The oligomer appears to be broadly compatible with fluoropolymers, especially perfluoropolymers, so large concentrations of
15 oligomer may be used if desirable properties can be so obtained. When the fluoropolymer is an elastomer, oligomer concentrations of 2-50 phr (parts per hundred of resin) may be used. Concentrations of 5-30 phr are preferred. Concentrations of 5-20 phr are most preferred. When the fluoropolymer is a plastic, oligomer concentrations of 2-150 and even 2-400 phr can be used.
20 Preferred concentrations vary with the fluoroplastic and the purpose, but generally 5-100 phr are preferred and 5-30 phr are most preferred.

The plasticized fluoropolymers of this invention are distinguished from solutions or gels in that the plasticized fluoropolymers are dimensionally
25 stable under the force of gravity at room temperature. By "dimensionally stable" is meant that a substantially void-free (less than 1% voids) cylinder of plasticized fluoropolymer with 2.5 cm diameter and 10 cm height, standing unsupported on a solid surface, does not sag or slump or otherwise change shape perceptibly within 4 hr. Moreover, the mechanical properties of the plasticized fluoropolymers may be readily measured by testing methods appropriate for the
30 unplasticized fluoropolymers or articles fabricated therefrom.

Methods of incorporating the high-boiling, highly-fluorinated, polycyclic alkane, e.g., fluoroalicyclic oligomer or phen-oligomer, into a fluoropolymer can be any of the mixing, blending, or compounding techniques known in the art and appropriate to the properties of oligomer and
35 fluoropolymer. When the fluoropolymer is an elastomer, oligomer may be

incorporated using conventional techniques for such materials, mixing on standard rubber processing equipment such as two-roll rubber mills or internal mixers. This may be done separately or in conjunction with the compounding of curatives, fillers, acid acceptors, processing aids, or other additives into the elastomer as needed to obtain a compound that can be cured to desired final properties. When the fluoropolymer is a melt-fabricable plastic, conventional melt blending techniques using equipment such as but not limited to twin-screw extruders, single-screw extruders, or internal mixers may be used to incorporate oligomer into the fluoropolymer. Alternatively or additionally, oligomer may be deposited on the fluoropolymer particles or pellets from solution in a relatively volatile solvent. When the fluoropolymer is not melt-processible, means of distributing oligomer uniformly throughout the fluoropolymer matrix are more limited and deposition from solution on the fluoropolymer particles before fabrication is particularly suitable. In any event, the plasticizer can be combined with the fluoropolymer to give a substantially void-free composition. Pigments, fillers, and other additives conventionally used may also be incorporated into fluoroplastics plasticized with oligomer.

Methods of fabricating articles from fluoroelastomers plasticized with the high-boiling, highly-fluorinated, polycyclic alkane, e.g., fluoroalicyclic oligomer or phen-oligomer, can be any of those known in the art. Methods of fabricating articles from fluoroplastics plasticized with oligomer can include most of the extrusion, injection molding, compression molding, and transfer molding techniques known in the art. However, high-temperature fabrication techniques that do not include the application of pressure may not be suitable if the temperature is high enough to volatilize the oligomer, although relatively thin sections might tolerate oligomer escape without damage if enough oligomer is retained to have the desired plasticizing effect. In other words, the fabricated article is of the fluoropolymer plasticized with highly-fluorinated, polycyclic alkane.

In addition to having the utility of forming fabricated articles from plasticized fluoropolymer compositions of the present invention, the plasticized fluoropolymer composition may also be used to bond at least two fluoropolymer surfaces of at least one article together by having the composition interposed between and in contact with the two surfaces, the fluoropolymer of the plasticized composition being the same or different from the fluoropolymer

of the two surfaces, followed by heating the composition to bond the surfaces one to the other through or via the composition without appreciable permanent deformation of the article. Generally this utility will be carried out with multiple surfaces of a single article or one or more surfaces of a plurality of articles in order to bond such articles together. The steps of interposing the composition between and in contact with the surfaces and heating the composition to effect the bonding can be carried out in any sequence or simultaneously. Normally, some pressure will be involved to force the surfaces being bonded towards one another to achieve intimate contact with the composition interposed there between but the pressure should be not so high as to cause permanent deformation of the articles during the heating of the composition. As one skilled in the art will recognize, various confining or restraining devices may be used to help prevent flow during this operation.

In this utility the plasticized fluoropolymer composition acts as an adhesive to bond the fluoropolymer surfaces together. In one embodiment the composition can be in particulate form distributed between the surfaces. In another embodiment, the plasticized fluoropolymer composition can be in a fabricated form such as a wafer or ribbon interposed between the surfaces to be bonded together. In either case, the composition acts upon heating to bond the surfaces together. The composition in the particulate form, if not a cured fluoroelastomer composition, can coalesce during the heating step to form a substantially void-free adhesive layer, the same as when the plasticized fluoropolymer composition in the form of a fabricated article is used to bond surfaces together. If the composition is an uncured fluoroelastomer composition, it can be cured during the bonding procedure.

The heating of the plasticized fluoropolymer composition in this adhesive utility can be accomplished by conventional means. The composition may be preheated before it is interposed between the surfaces to be bonded together, followed by heating to effect the bonding of the surfaces together. When the fluoropolymers of the surface and of the plasticized composition are crystalline polymer, such polymers will have melting temperatures, and to effect selective melting of the plasticized fluoropolymer composition and non-melting of the fluoropolymer surfaces, it is preferred that the fluoropolymer composition have a lower melting temperature than the melting temperature than either of the fluoropolymer surfaces to be bonded together.

EXAMPLES

The invention is illustrated by the following non-limiting examples.

Example 1

5 A hydrogen-containing fluoroelastomer generally of the type described in Example 17 of U.S. Patent 4,035,565 except that the bromine-containing monomer was 4-bromo-3,3,4,4-tetrafluorobutene-1 was compounded with MT carbon black (30 phr) and phen-oligomer as the fluoroalicyclic oligomer (5 phr) on a two-roll rubber mill at 75°C. The oligomer
10 was heated gently to a honey-like viscosity to enable it to be poured. Piston rheometry was carried out at 90°C and 110°C over the shear rate range 1-1000 sec⁻¹. Melt fracture was observed at 1, 5, and 10 sec⁻¹ but the extrudate was smooth at rates of 50-1000 sec⁻¹. A control with no oligomer exhibited melt fracture under all conditions.

15

Example 2

A hydrogen-containing fluoroelastomer of the type described in Comparative Example A of U.S. Patent 4,973,633 was compounded with 30 phr of MT carbon black and with 5 or 10 phr of phen-oligomer as the fluoroalicyclic oligomer. Extrudate from piston rheometry at 110°C was smooth over the entire
20 shear rate range 1-1000 sec⁻¹ for the compound with 10 phr oligomer, was smooth only at 1000 sec⁻¹ for the compound with 5 phr oligomer, and exhibited melt fracture at all shear rates except 10 sec⁻¹ for the control with no oligomer.

Example 3

Fluoroalicyclic oligomer (phen-oligomer) was compounded with
25 the fluoroelastomer of Example 1 and other ingredients on a two-roll rubber mill at 75°C in the proportions given in Table 1. Piston rheometry at 110°C showed melt fracture for the control (Sample A) at all shear rates over the range 1-1000 sec⁻¹ and no melt fracture over the same shear rate range for Sample D with an oligomer concentration of 20 phr. The compound was converted to a form
30 suitable for physical testing by compression molding into sheet stock 15 cm square and 1.9 mm thick. The sheet was press-cured at 177°C for 30 min, then post-cured at 232°C for 24 hr in a circulating air oven. Specimens were die-cut from the sheet as called for by the test methods following. Tensile properties (ASTM D-412), tear strength (ASTM D-470), compression set at 200°C for 70
35 hr (ASTM D-395), and hardness (ASTM D-395) were measured. Results are

also given in Table 1. It is seen that oligomer enhances tensile elongation and both tensile and tear strengths while reducing modulus and compression set, the latter especially at oligomer concentrations of 5-10 phr. These results illustrate a plasticizing effect without adverse effect, and even with beneficial effect, on important properties.

Table 1. Fluoroelastomer Compounds with Oligomer

<u>Ingredients (parts)</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Fluoroelastomer	100	100	100	100
Oligomer	0	5	10	20
MT carbon black	30	30	30	30
Ca(OH) ₂	4	4	4	4
Triallyl isocyanurate ^a	4	4	4	4
"Luperco" 101XL ^b	4	4	4	4
<u>Properties</u>				
Tensile strength (psi)	2000	2150	2200	2450
Elongation at break (%)	60	85	195	230
Modulus M100 (psi)	920	75	780	660
Tear strength (pli)	12	14	13	14
Hardness (Shore A)	75	75	74	74
Compression set (%)	42	35	37	40

^a Diak[®] No. 7 curing agent, Du Pont Co.

^b Luperco 101XL is 45% 2,5-dimethyl-2,5-di-(t-butylperoxy) hexane on calcium carbonate substrate, Lubrizol Co.

Example 4

An experimental partially-crystalline TFE/HFP copolymer resin was compounded with 15 and 30 phr of phen-oligomer as the fluoroalicyclic oligomer in a laboratory-scale internal mixer at 250°C. This TFE/HFP copolymer had molar composition of about 81.5/18.5 based on infrared measurement as described in U.S. Patent 4,380,618, but using peak absorbances of bands found at 10.18 mm and at 4.25 mm, and melt viscosity of 1.2×10^3 Pa·s (U.S. Patent 4,380,618). Piston rheometry was carried out at 225° and

250°C over the shear stress range of about 0.01-0.28 MPa to assess the effect of oligomer incorporation on viscosity of the TFE/HFP copolymer resin. Results presented graphically in Fig. 4 for the testing at 250°C show significant effect of oligomer.

5

Example 5

To 15 g of a TFE/PPVE copolymer powder prepared by the method of European Patent 271,243 and having molar composition of about 98.5/1.5 were added 50 ml of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113). A 32 wt% solution of fluoroalicyclic oligomer (phen-oligomer) in CFC-113 was added in amounts to give the concentrations of oligomer in the copolymer resin shown in Table 2. The CFC-113 was evaporated on a rotary evaporator under reduced pressure, and the material was then further dried at 80°C for 0.5 hr in a circulating air oven. The melt flow rate (MFR) was then determined according to ASTM D-3307, with the following results showing the plasticizing effect of oligomer.

15

Table 2. Plasticized TFE/PPVE Copolymer

Oligomer Conc. (phr)	MFR (g/10 min)	Tensile Properties			
		TS (psi)	Elong. (%)	Mod. (psi)	
20	0	1.82	3617	327	22,849
	10	2.43			
	20	3.35			
	30	3.84	3261	384	19,057
	40	5.21			
25	50	7.68			
	100	21.30			

Example 6

This example demonstrates the benefit of added fluoroalicyclic oligomer in ram extrusion of suspension-polymerized (granular) PTFE. Oligomer (Phen-oligomer) was added to PTFE resin as part of the non-aqueous phase during solvent-aided-pelletization of the PTFE, as follows. To 300 g of fine-cut granular PTFE with average particle size of about 30 µm (Teflon® TFE fluorocarbon resin grade 7A, Du Pont Company) in a 2-liter resin kettle were added 1000 ml of water and 111 ml of a solution of oligomer in CFC-113. The

35

concentration of the oligomer solution was varied to give the added amounts indicated in Table 3. The mixture was stirred at 1200 rpm for 5 min, free water was drained off, and the PTFE pellets were dried in a circulating air oven at 100°C for 4 hr.

5 A horizontal ram extruder with a 0.25-inch (0.64-cm) die and five heated zones set at 327°, 382°, 382°, 382°, and 260°C in the order of feed to die was used. A constant volume of resin was fed for each cycle. The extrusion rate was varied by adjusting the dwell time for the ram in the forward position, i.e., the shorter the ram-forward time, the faster the extrusion rate. The control
10 without oligomer was extruded first. A smooth rod was obtained with a ram-forward time of 7 sec, but a ram-forward time of 5 sec gave a rough rod with visible lines at charge boundaries (charge fracture or poker chipping). The pellets containing 5 or 17 phr of oligomer could be extruded into smooth, poker chip free rod at either 5 or 7 sec ram-forward time. Dumbbell-shaped specimens
15 were machined from the rod for measurement of tensile properties, also shown in Table 3. As shown by the data, as little as 5 phr of oligomer facilitated the ram extrusion by allowing faster extrusion and yielded superior properties. Lesser and greater amounts of oligomer will be effective to impart improved ram extrudability to the resin. Pellets containing 17 phr of oligomer could also
20 be extruded into smooth, poker chip free rod at both ram-forward times, but tensile measurements were not made.

Table 3. Ram Extrusion of PTFE Containing Oligomer

25	<u>Sample</u>	<u>Oligomer</u>		<u>Dwell Time (sec)</u>	<u>Tensile Properties</u>	
		<u>(g)</u>	<u>(phr)</u>		<u>TS (psi)</u>	<u>Elong. (%)</u>
	A	0	0	7	4006	242
	B	0	0	5	2507	137
	C	15	5	7	5022	266
	D	15	5	5	4926	259

30

Example 7

A sample of phen-oligomer was fractionated into three cuts of approximately equal volume by vacuum distillation. The cuts had glass transition temperature T_g of -22.6°, 26.0°, and 62.6°C as measured by
35 differential scanning calorimetry (DSC) and were identified as Cut 1, 2 and 3 in

the stated order. The whole sample of oligomer and the three cuts were added in various concentrations to a TFE/PPVE copolymer similar to that of Example 5 except for melt flow rate by compounding the oligomer with copolymer cubes in an internal mixer (System 40 Controlled Torque Rheometer with Rheomix®
5 3000-E mixer, Haake Buchler Instruments). MFR was determined at 372°C according to ASTM D-1238 using a 5 kg weight. Plaques approximately 15 cm square and 3.2 mm thick were molded by the following procedure. A brass frame of appropriate dimensions was placed on a piece of polyimide film (KAPTON®, DuPont Company). The blend (135 g) of copolymer and oligomer
10 was placed in the square opening of the frame and was distributed uniformly. The filled frame was covered with another piece of polyimide film, and the assembly was placed between the platens of a laboratory press heated to 327°C. The press was closed to make contact with the assembly at an initial load of 3000 lb (1364 kg) and held in that position for 8 min. The load was increased to
15 10,000 lb (4545 kg) and immediately released. This load cycle was repeated three times. The load was again applied at 10,000 lb and held for 2 min, and then at 20,000 lb (9091 kg) for 2 min. The assembly was removed from the hot press and was immediately transferred to another press with water-cooled platens at 25°C and held under 10,000 lb load for 4 min. The assembly was
20 removed from the press, the polyimide film was stripped off the assembly and the plaque was removed from the frame. Tensile properties were determined according to ASTM D-1457 and flex modulus was determined according to ASTM D-790, all at 22°C. Sample compositions and test results are shown in Table 4. Concentrations in this example are in wt%. With the exception of two
25 samples, the measured concentrations of oligomer were determined from weights of the samples as discharged from the internal mixer, before and after heating for 24 hr at 350°C. The measured concentrations for the compositions containing 20 wt% of whole oligomer and 10 wt% of Cut 3 were determined on the molded plaques. All cuts increase MFR in all concentrations, which increase
30 would facilitate melt processing. Note the unusual results for Cut 3, with both flex modulus and MFR increasing with added oligomer fraction. A piece of several of the plaques was tested by dynamic mechanical analysis (Dynamic Mechanical Analyzer Model 983, TA Instruments; DMTA, Polymer Laboratories). Results show that the second order transition occurring near
35 100°C in the neat TFE/PPVE copolymer, usually identified as the alpha

transition, is shifted to lower temperature in the blends with fluoroalicyclic oligomer. This is consistent with the expected effect of a plasticizer. The magnitude of the shift varied with oligomer sample, and was greatest for Cut 1, least for Cut 3. The shift for Cut 2 was intermediate and about the same as the shift for the whole oligomer. However, the data indicate that the real part of the complex bending modulus for the blends, in a temperature range below the transition, is greater than the corresponding value for the neat TFE/PPVE copolymer at the same temperature. These observations are consistent with the flex modulus data in Table 4.

Flex life was measured for three of the plasticized samples following the method of ASTM D-2176 using a 4 lb (1.8 kg) weight and a #8 spring. For these measurements, a film 0.7 mm thick was used, molded by the general procedure used for the 3.2 mm plaques above. Each sample was tested five times and results were averaged. Using the flex life of the TFE/PPVE copolymer without added oligomer as reference, the compound with 20 wt% of whole oligomer had flex life of 1x, the compound with 10 wt% of Cut 2 had flex life of 3x, and the compound with 10 wt% of Cut 1 had flex life of 22x.

Table 4. Data Summary for Example 7

<u>Oligomer</u>	<u>Concentration (wt%)</u>		<u>Tensile Properties</u>		<u>FlexMod (MPa)</u>	<u>MFR (g/10 min)</u>
	<u>Added</u>	<u>Meas.</u>	<u>TS (psi)</u>	<u>El. (%)</u>		
None	0	0.8	3177	281	621	15.9
Whole	10	9.7	2703	140	643	20.0
Whole	20	18.1	2187	37	408	29.0
Whole	30	28.5	1640	22	270	50.4
Cut 1	10	9.3	2580	259	368	20.1
Cut 1	25	18.7	1290	108	134	33.0
Cut 2	10	10.4	2713	125	623	20.8
Cut 2	25	23.9	2574	3	585	38.9
Cut 3	10	10.5	3145	223	931	21.4
Cut 3	25	25.0	1987	2	1063	40.3

20

Example 8

A supply of a modified PTFE resin prepared by the emulsion polymerization process (TEFLON® TFE fluorocarbon resin grade 6C, DuPont

Company) was conditioned at 7°C. Such resin prepared by emulsion polymerization is also well known as PTFE fine powder. A 25 wt% solution of phen-oligomer in perfluoro(2-butyl tetrahydrofuran) (Fluorinert® FC-75, 3M Company) was prepared. An amount of the solution calculated to yield an oligomer/PTFE blend that was 22 wt% oligomer was added to 60 g of the PTFE resin in a wide-mouth bottle. The bottle was sealed, and the solution and resin were blended for 1 hr on a bottle roller. The bottle was allowed to stand for 24 hr, rolled for 4 hr, allowed to stand for another 24 hr, and finally rolled for another 4 hr. Then, the bottle was opened, covered with cheese cloth, and the FC-75 was removed from the blend by heating at 93°C for 12 hr. The oligomer/PTFE blend was then cooled to room temperature. A second oligomer/PTFE blend containing 38 wt% oligomer was prepared by the same procedure. The two blends were paste extruded as well known in the art, without conventional lubricant, to make a beading using a capillary rheometer. Cylinder diameter was about 2.1 cm and die orifice diameter was 3.0 mm, yielding a reduction ratio of about 50. Extrusion temperature was 93°C. Ram speed was 10 mm/min. Part of each beading sample was sintered in a circulating air oven at 380°C for 4 hr. These sintering conditions, which are more severe than required to sinter the PTFE resin, were chosen with the intent of driving most if not all of the phen-oligomer out of the beading. A control beading was made without oligomer, using the same PTFE resin and 18.5 wt% Isopar® G (Exxon Corporation) as extrusion lubricant. The control was extruded at room temperature, and was dried at 93°C for 30 min. Tensile properties of the various beadings are summarized in Table 5.

Table 5. Summary of Results for Example 8

Oligomer		<u>Tensile Properties</u>	
<u>Conc. (wt%)</u>	<u>Sintered</u>	<u>TS (psi)</u>	<u>Elong. (%)</u>
20	No	526	22
20	Yes	994	69
38	No	50	90
38	Yes	965	56
Control	No	148	43

The PTFE beading containing 20 wt% oligomer exhibited extremely high "green" (unsintered) strength which is valuable in applications when the unsintered PTFE must be subjected to rough handling. Thus, for unsintered PTFE fine powder, not only does the oligomer provide valuable plasticization properties, but also adds value to the paste extrusion thereof. Lubricant conventionally used and volatilized from the extrudate before sintering need not be used in favor of using oligomer as the paste extrusion lubricant. Sintering conditions can be chosen to achieve coalescence of the PTFE and retain most of the oligomer, e.g., by using short sintering time, thereby obtaining a plasticized composition after sintering. Moreover, the green paste extrudate may be useful in some applications, such as sealants or gasketing. Preferably, the amount of high-boiling, highly-fluorinated, polycyclic alkane used for this purpose (effective for rendering the PTFE fine powder paste extrudable) will be from about 15 wt% to about 50 wt% based on the combined weight of poly-cyclic alkane and PTFE.

CLAIMS

1. A plasticized fluoropolymer composition, comprising a fluoropolymer derived from at least one monomer selected from the group consisting of fluoroolefins and fluorinated vinyl ethers of the formula
5 $CY_2=CYOR$ or $CY_2=CYOR'OR$, where Y is H or F, and -R and -R' are independently completely-fluorinated or partially-fluorinated alkyl and alkylene groups containing 1-8 carbon atoms, said fluoropolymer plasticized with about 2-400 phr of high-boiling, highly-fluorinated, polycyclic alkane, said composition being dimensionally stable at room temperature and substantially
10 void-free.
2. The composition of Claim 1, wherein the polycyclic alkane is fluoroalicyclic oligomer.
3. The composition of Claim 2, wherein the fluoroalicyclic oligomer is phen-oligomer.
- 15 4. The composition of Claim 1, wherein the plasticizer concentration is about 2-150 phr.
5. The composition of Claim 4, wherein the fluoropolymer is an elastomer and the plasticizer concentration is about 2-50 phr.
6. The composition of Claim 5, wherein the plasticizer
20 concentration is about 5-30 phr.
7. The composition of Claim 6, wherein the plasticizer concentration is about 5-20 phr.
8. The composition of Claim 5, wherein the elastomer is a hydrogen-containing fluoroelastomer
- 25 9. The composition of Claim 5, wherein the elastomer is a perfluoroelastomer.
10. The composition of Claim 1, wherein the fluoropolymer is plastic.
11. The composition of Claim 10, wherein the plasticizer
30 concentration is about 5-100 phr.
12. The composition of Claim 11, wherein the plasticizer concentration is about 5-30 phr.
13. The composition of Claim 10, wherein the plastic fluoropolymer is a TFE polymer.

14. Process for bonding at least two fluoropolymer surfaces of at least one article together, comprising interposing a plasticized fluoropolymer composition comprising a fluoropolymer derived from at least one monomer selected from the group consisting of fluoroolefins and fluorinated vinyl ethers of the formula $CY_2=CYOR$ or $CY_2=CYOR'OR$, where Y is H or F, and -R and -R' are independently completely-fluorinated or partially-fluorinated alkyl and alkylene groups containing 1-8 carbon atoms, said fluoropolymer plasticized with about 2-400 phr of high-boiling, highly fluorinated, polycyclic alkane, between and in contact with said two surfaces, the fluoropolymer of said composition being the same or different from the fluoropolymer of said surfaces, heating said composition to bond said surfaces one to the other through said composition without appreciable permanent deformation of said article.

15. Process of claim 14 wherein said composition is in the form of a fabricated article.

16. Process of claim 14 wherein the fluoropolymer composition has a lower melting temperature than the melting temperature of the fluoropolymer constituting said surfaces.

17. A process comprising preparing a composition comprising unsintered polytetrafluoroethylene fine powder with an amount of high-boiling, highly-fluorinated, polycyclic alkane effective to render said polytetrafluoroethylene fine powder paste extrudable, and paste extruding said composition.

18. A process comprising preparing a composition comprising unsintered polytetrafluoroethylene granular resin with an amount of high-boiling, highly-fluorinated, polycyclic alkane effective to facilitate ram extrusion of said resin, and ram extruding said composition.

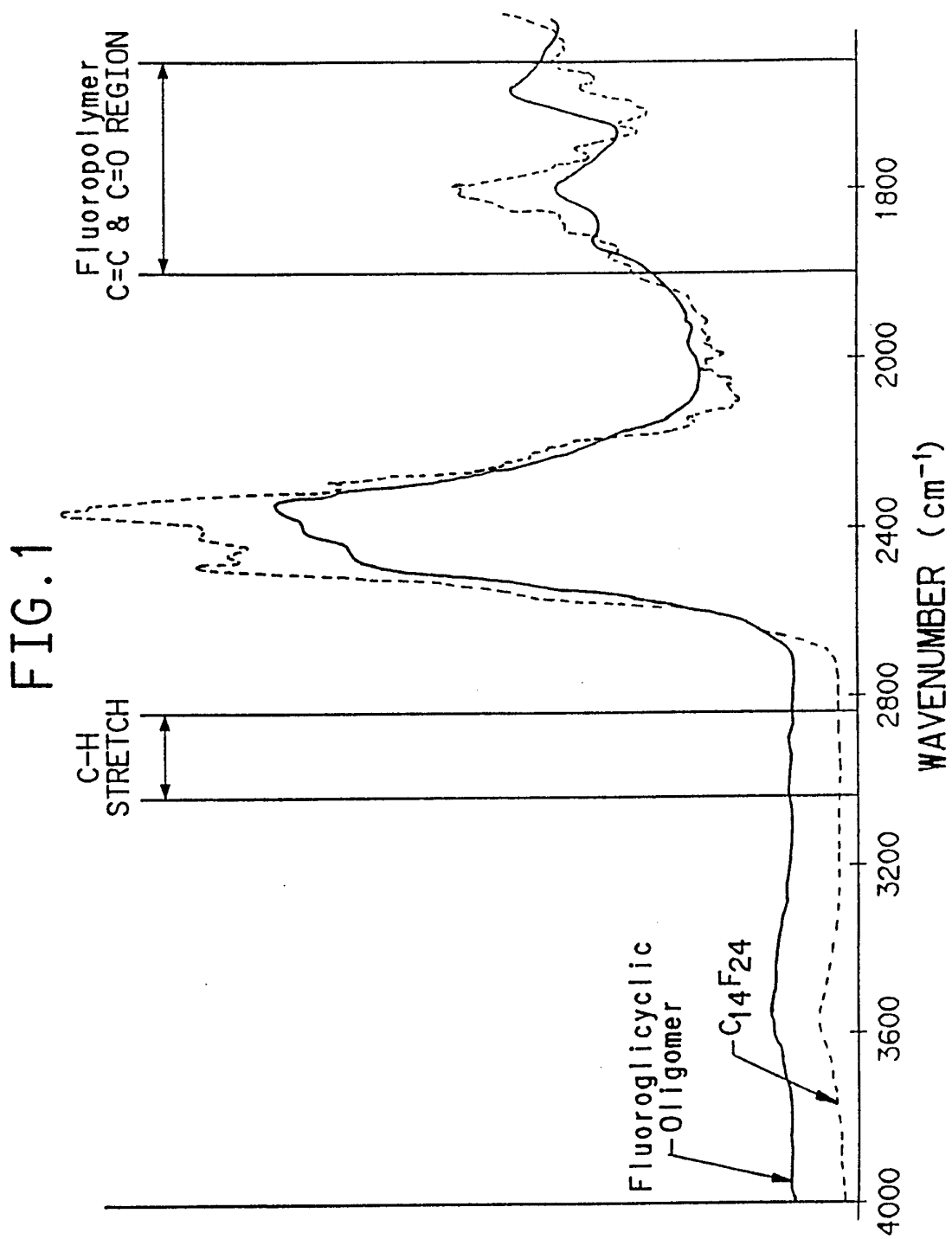


FIG. 2

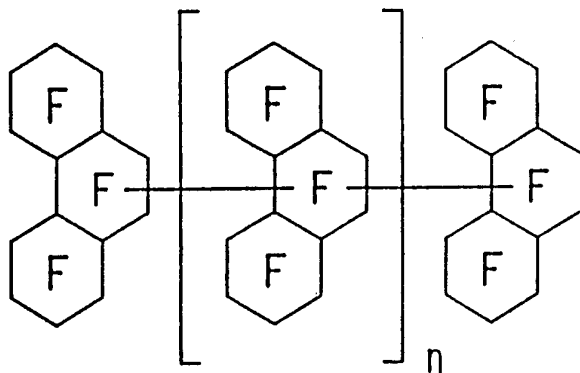


FIG. 3

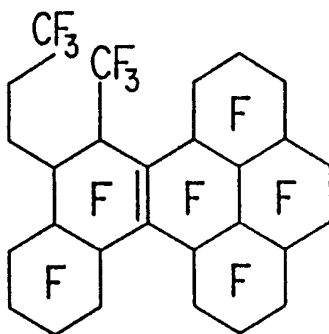
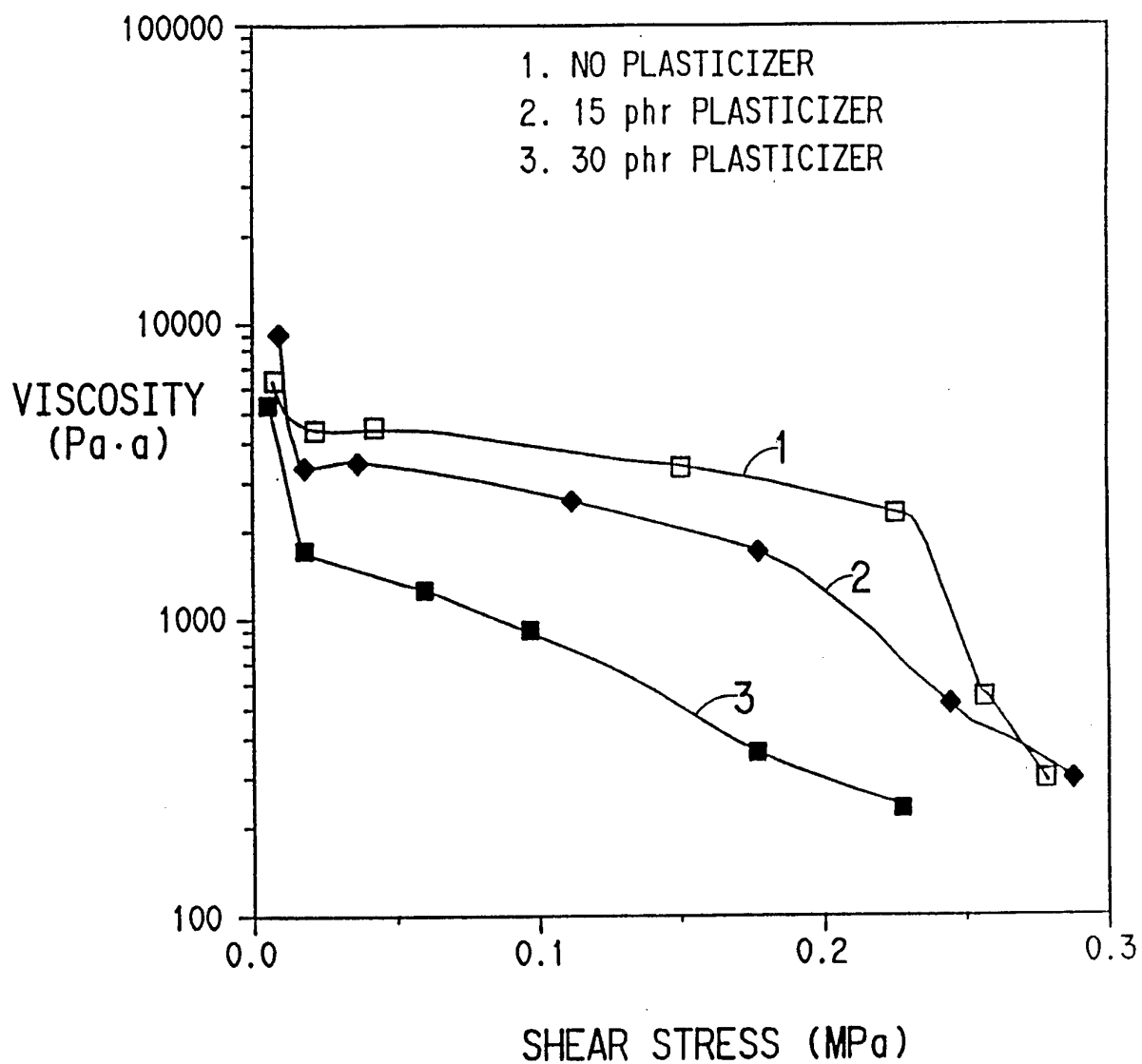


FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07788

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 27/22; C08K 5/02

US CL :428/421,422; 524/462

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/421,422; 524/462

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,403,036 (HINDERSINN et al) 24 SEPTEMBER 1968. See entire document.	1-16
Y	US, A, 4,171,977 (HASEGAWA et al) 23 OCTOBER 1979. See entire document.	1-16

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	*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
A document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*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
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)	*G* document member of the same patent family
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	

Date of the actual completion of the international search

26 JANUARY 1994

Date of mailing of the international search report

16 FEB 1994

Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/07788

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

(Form PCT/ISA/206 Previously Mailed.)

Group I: Claims 1-16 drawn to a fluoropolymer composition and a process of bonding classified in Class 428 subclass 411.1.

Group II: Claim 17 drawn to a process of paste extruding classified in Class 264 subclass 239.

Group III: Claim 18 drawn to a process of ram extruding classified in Class 264 subclass 239.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.