

COPOLYMERS OF VINYLIDENE FLUORIDE AND
HEXAFLUOROPROPYLENE HAVING REDUCED
EXTRACTABLE CONTENT AND IMPROVED SOLUTION CLARITY

This application claims the benefit of
provisional application serial number 60/038,346 filed
Feb. 28, 1997.

BACKGROUND OF THE INVENTION

This invention relates to compositions of matter
classified in the art of chemistry as fluoropolymers,
more specifically as copolymers of vinylidene fluoride
(VDF), more specifically as copolymers of vinylidene
fluoride and hexafluoropropylene (HFP), still more
specifically as copolymers of VDF and HFP having
reduced extractable content, longer gel times and
improved solution clarity, to novel compositions of
matter and articles of manufacture containing such
copolymers, as well as to processes for the
preparation and use of the copolymers, of compositions
of matter containing such copolymers and of the
articles of manufacture containing such copolymers.

VDF/HFP copolymers are well known and are used for their thermoplastic engineering properties, chemical resistance and inertness toward degradation. They may be found in applications such as chemically resistant piping, gasketing, plenum cable jacketing, filtration and extraction membranes and in the construction of lithium batteries.

The present invention provides VDF/HFP copolymers containing up to about 24 weight % (12 mole%) HFP having among other improved properties, substantially improved solution clarity, longer gel times and reduced extractables as these terms are defined hereinafter.

The process used to make the instant copolymers requires one ratio of VDF and HFP for the initial fill of the reactor, and a different ratio of VDF and HFP during a subsequent continuous feed of the monomers. Any particular desired average HFP content in the copolymer product has corresponding particular initial fill and subsequent feed ratios. The uniformity of compositions prepared this way provide unique and useful properties in comparison to VDF/HFP copolymers described in the prior art.

DISCLOSURE OF PRIOR ART

Rexford in U.S. Pat. No. 3,051,677 described VDF/HFP copolymers of HFP content 30 to 70 wt% (15 to 50 mol%) which showed utility as elastomers. To make the copolymers, a batch process with certain initial ratios of VDF and HFP, and a continuous process with fixed ratios of VDF and HFP throughout the process

were described. The processes described were such that polymers lacking the improved solution clarity, longer gel times and low extractables of the present invention were made.

Lo in U.S. Pat. No. 3,178,399 described VDF/HFP
5 copolymers of HFP content of 2 to 26 wt% (1 to 13 mol%) which showed a numerical value for the product of the tensile strength (psig) and percent reversible elongation of at least 1,000,000. A batch process with certain initial ratios of VDF and HFP, or,
10 alternately, a semicontinuous process with fixed ratios of VDF and HFP throughout the process were used to make the copolymers. The processes discussed were such that copolymers lacking the improved solution clarity, longer gel times and low extractables of the present invention copolymers were made.
15

Moggi, et al. in Polymer Bulletin 7, 115-122 (1982) analyzed the microstructure and crystal structure of VDF/HFP copolymers by nuclear magnetic resonance and x-ray diffraction experiments. The
20 copolymers of up to 31 wt% (up to 16 mol%) HFP were made in a batch emulsion process which was carried only to low conversion. While the low conversion batch process is capable of producing copolymers having solution clarity and low extractables, no such
25 properties are described. It is not a practical process for industrial use because of the low conversions required to make the materials. In addition, no detailed polymerization examples were offered.

Bonardelli et al. in Polymer, vol. 27, 905-909 (June 1986) studied the glass transition temperatures of VDF/HFP copolymers having HFP content up to 62 wt.% (up to 41 mol%). The glass transition temperatures were correlated to the overall HFP content in the copolymers. In making the copolymers for analysis, a semicontinuous emulsion process was used which employed different VDF/HFP ratios for the initial fill of the reactor and for the subsequent continuous feed of monomers. Although reference was made to the use of reactivity ratios to set the VDF/HFP ratio for the initial fill, no detailed polymerization examples were offered, and no mention of copolymers having solution clarity, gel times and low extractables comparable to that of the copolymers of the present invention was made.

Pianca et al. in Polymer, vol. 28, 224-230 (Feb. 1987) examined the microstructure of VDF/HFP copolymers by nuclear magnetic resonance, and the microstructure determinations were used to explain the trend in glass transition temperatures of the copolymers. The synthesis of the copolymers involved a semicontinuous emulsion process which used different VDF/HFP ratios for the initial fill of the reactor and for the subsequent continuous feed of monomers. No detailed synthesis examples were provided, and there was no discussion of copolymers having improved solution clarity, longer gel times and low extractables as provided by the copolymers of the present invention.

Abusleme et al. in Eur. Pat. Appl. No. 650,982 A1 showed an emulsion process to make polymers and copolymers of fluorinated olefins optionally with one or more non-fluorinated olefins. The process relied on photochemical initiation of polymerization so that lower temperatures and pressures could be used than those used for thermally initiated processes. While there was general mention of the structural regularity of the resulting polymers, the only evidence of regularity concerned poly(vinylidene fluoride) homopolymer, and no claims were made as to regularity of composition. Examples of VDF/HFP copolymerization were given, but no discussion of the solution extraction properties of the copolymers was given, and there was no relation made between physical properties and the structure of the VDF/HFP copolymers.

Morgan in U.S. Pat. No. 5,543,217 disclosed uniform tetrafluoroethylene/hexafluoropropylene copolymers (TFE/HFP copolymers) made by a semicontinuous emulsion process. Uniformity was simply defined as there being a low proportion of adjacent HFP units in the polymer chains; there was no disclosure of the disposition of TFE and HFP units otherwise, and there was no discussion of VDF/HFP copolymers or the properties to be expected therefrom.

U.S. Patent 2,752,331 describes the synthesis of VDF/chlorotrifluoroethylene (CTFE) copolymers having a high uniformity of comonomer distribution in its molecular chains.

Baggett and Smith in *High Polymers*, Vol. XVIII,

Ham, John Wiley (1964), Chapter X, Copolymerization, pp. 587 et seq., particularly at pp. 593 and 610 describe the synthesis of uniform composition distribution copolymers of vinylidene chloride and vinyl chloride and of vinyl chloride and vinyl acetate.

None of these references teaches or suggests a way to obtain VDF/HFP copolymers having solvent solution clarity and fluidity, longer gel times and low extractables comparable to the VDF/HFP copolymers of the instant invention or that such properties are attainable from VDF/HFP copolymers.

SUMMARY OF THE INVENTION

The invention provides in a first composition aspect a copolymer of vinylidene fluoride and hexafluoropropylene containing a maximum of about 24 weight percent hexafluoropropylene, having solutions of improved clarity and fluidity; for the copolymers having up to about 8 weight percent nominal HFP content, having weight percent extractables within plus or minus 1.5% of the percent by weight extractables calculated by an equation selected from the group consisting of:

- a) $\text{Wt.}\% \text{ Extractables} = 1.7(\text{HFP mole}\%) - 3.2$, and
- b) $\text{Wt.}\% \text{ Extractables} = -1.2 + 1.5(\text{HFP mole}\%) - 8 \times 10^{-6}(\text{Mn})$,

and for the copolymers having greater than about 8 weight percent nominal HFP content, having a DSC (differential scanning calorimetry) melting point at least 2.5°C lower than the DSC melting point of copolymers having the same nominal weight percent HFP

prepared by methods for which the prior art provides detail.

5 The tangible embodiments of this first composition aspect of the invention are straw colored to colorless semi crystalline solids having melting points, as determined by differential scanning calorimetry (DSC), lower than VDF/HFP copolymers having the same nominal HFP percentage content prepared by processes reported in detail in the prior art.

10 The tangible embodiments of this first composition aspect of the invention also possess longer gelation times from solution than VDF/HFP copolymers having the same nominal HFP content prepared by processes reported in detail in the prior art.

15 The aforementioned physical characteristics taken together with the method of synthesis positively tend to confirm the structure and the novelty of the compositions sought to be patented.

20 The tangible embodiments of the first composition aspect of the invention have the inherent applied use characteristics of being suitable for paint and powder coating vehicles and as chemically resistant shaped objects and films both supported and unsupported.

25 Particular mention is made of copolymers of the first composition aspect of the present invention having from about 2 weight% HFP content to about 8 weight% HFP, still more particularly copolymers having about 3 to 6 weight% HFP which possess the inherent applied

30 use characteristics of being particularly suitable as

polymeric separators and polymeric electrode matrices for batteries, particularly lithium batteries. The prior art, see for example U.S. 5,296,318 has reported lithium batteries made from PVDF/HFP copolymers having from 8% to 25% by weight HFP. It is understood that the copolymers of the present invention having HFP content in that range are suitable for use in such batteries and would represent an improvement therein. Such improved batteries are also contemplated by the invention as equivalents.

Particular mention is also made of copolymers of the first composition aspect of the invention having from about 7 weight percent HFP content to about 15 weight percent HFP content, more particularly copolymers having about 10 weight percent HFP content which possess the inherent applied use characteristic of being suitable as flame resistant insulation for wire and cable.

Still further mention is made of copolymers of the first composition aspect of the invention having greater than about 15 weight percent HFP content, still more particularly of copolymers having about 16% by weight or greater HFP content which have the inherent applied use characteristic as clear, flexible, chemically resistant films.

The invention provides in a second composition of matter aspect, an improved article of manufacture comprising an electrochemical cell having a positive electrode, an absorber separator and a negative electrode wherein at least either one of the electrodes comprises a vinylidene fluoride polymer

having an electrolyte material combined therewith or said absorber separator comprises a vinylidene fluoride polymer having an electrolyte material combined therewith wherein the improvement comprises the polyvinylidene fluoride polymer consisting essentially of a vinylidene fluoride/hexafluoropropylene copolymer as defined in the first composition aspect of the invention.

Special mention is made of embodiments of the second composition of the invention wherein the VDF/HFP copolymer has a hexafluoropropylene content of from about 2 weight % hexafluoropropylene to about 8 weight % particularly those having from about 3 weight % to about 6 weight % hexafluoropropylene, still more particularly, those having about 3 weight % hexafluoropropylene.

The electrochemical cells of which the second composition of matter aspect of this invention is an improvement are described in PCT Application WO 95/06332, European Patent Application 95 120 660.6-1215, published as number 730,316 A1 on September 4, 1996 and U.S. Patent 5,296,318. The disclosures of the PCT application, the European application and the U.S. Patent are hereby incorporated by reference. In addition to use of solution casting techniques for preparation of films for use in battery constructions as described in the aforementioned references, use of extrusion techniques to prepare such films and the

batteries fabricated therefrom are also contemplated.

It has also been noted that batteries fabricated from the PVDF-HFP copolymers of the present invention have better adhesion of the polymers to metallic portions of electrodes and higher use temperatures than batteries fabricated from PVDF-HFP copolymers having similar percentage HFP content synthesized by prior art processes described in sufficient detail for reproduction. It has also been observed that PVDF-HFP copolymers of the present invention provide batteries having improved electrical properties including the capability of higher discharge rates than batteries fabricated from PVDF-HFP copolymers of having similar percentage HFP content synthesized by processes described in the prior art in sufficient detail for reproduction.

The invention provides in a third composition aspect, a solution of a composition of the first composition aspect of the invention having improved solution clarity and fluidity.

Copolymers of vinylidene fluoride and hexafluoropropylene of up to about 24 wt% hexafluoropropylene are useful semicrystalline thermoplastics. As the HFP content increases in the materials, the crystallinity decreases, and, correspondingly, the flexibility and solvent sensitivity increase. Other properties change as well, such as the final melting point, which decreases with increasing HFP content. In high-purity applications such as membrane filtration or

extraction, lithium battery construction, high-transparency film from solution casting, and fluid storage and transport requiring low contaminant levels, it is desirable to have materials with low levels of extractables, little gel formation in the presence of solvent, and good clarity. The VDF/HFP copolymers provided here show lower extractables, improved solution properties, improved clarity and fluidity, and lower melting points in comparison to the nonuniform VDF/HFP copolymers of otherwise similar HFP content and manufacture known in the prior art.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a comparison of the final differential scanning calorimeter/(DSC) melting point of copolymers of the invention with DSC melting points of prior art compounds whose synthesis is described in detail.

Figure 2 shows the effect on HFP level on polymer extractibles in dimethyl carbonate (DMC) at 40°C for copolymers of the invention and copolymers of the prior art whose synthesis is described in detail.

Figure 3 shows the relationship between HFP content and log of gelation time from solution (20 wt% in propylene carbonate) of copolymers of the present invention and of copolymers of the prior art having sufficient synthesis detail for reproduction.

DETAILED DESCRIPTION

The invention provides copolymers of vinylidene fluoride and hexafluoropropylene having hexafluoropropylene content of up to about 24 wt% and

having improved solution clarity and fluidity and reduced extractables. The copolymers are conveniently made by an emulsion polymerization process, but suspension and solution processes may also be used.

In an emulsion polymerization process a reactor is charged with deionized water, water-soluble surfactant capable of emulsifying the reaction mass during polymerization, paraffin antifoulant, vinylidene fluoride, hexafluoropropylene, chain-transfer agent to control copolymer molecular weight, and initiator to start and maintain the polymerization. To obtain the VDF/HFP copolymers of the present invention, the initial charge of VDF and HFP monomers is such that the amount of HFP is up to 48% of the combined weight of the monomers initially charged, and then VDF and HFP are fed continuously throughout the reaction such that the amount of the HFP is up to 24% of the combined weight of the monomers fed continuously. The VDF/HFP ratios are different in the initial charge and during the continuous feed, and each final polymer composition has definite and related ratios for the initial charge and continuous feed. The process uses total amounts of VDF and HFP monomers such that the amount of HFP used is up to about 24% of the combined total weight of the monomers.

The reactor is a pressurized polymerization reactor equipped with a stirrer and heat control means. The temperature of the polymerization can vary depending on the characteristics of the initiator used, but it is typically between 65° and 105°C, and

most conveniently it is between 75° and 95°C. The temperature is not limited to this range, however, and might be higher or lower if a high-temperature or low-temperature initiator is used. The VDF/HFP ratios used in the polymerization will be dependent on the temperature chosen for reaction. The pressure of the polymerization is typically between 2750 and 6900 kPa, but it can be higher if the equipment permits operation at higher pressure. The pressure is most conveniently between 3790 and 5860 kPa.

Surfactants used in the polymerization are water-soluble, halogenated surfactants, especially fluorinated surfactants such as the ammonium, substituted ammonium, quaternary ammonium, or alkali metal salts of perfluorinated or partially fluorinated alkyl carboxylates, the perfluorinated or partially fluorinated monoalkyl phosphate esters, the perfluorinated or partially fluorinated alkyl ether or polyether carboxylates, the perfluorinated or partially fluorinated alkyl sulfonates, and the perfluorinated or partially fluorinated alkyl sulfates. Some specific, but not limiting examples are the salts of the acids described in U.S. Pat. No. 2,559,752 of the formula $X(CF_2)_nCOOM$, wherein X is hydrogen or fluorine, M is an alkali metal, ammonium, substituted ammonium (e.g., alkylamine of 1 to 4 carbon atoms), or quaternary ammonium ion, and n is an integer from 6 to 20; sulfuric acid esters of polyfluoroalkanols of the formula $X(CF_2)_nCH_2OSO_3M$, where X and M are as above; and salts of the acids of

the formula $\text{CF}_3(\text{CF}_2)_n(\text{CX}_2)_m\text{SO}_3\text{M}$, where X and M are as above, n is an integer from 3 to 7, and m is an integer from 0 to 2, such as in potassium perfluorooctyl sulfonate. The surfactant charge is from 0.05% to 2% by weight on the total monomer weight used, and most preferably the surfactant charge is from 0.1% to 0.2% by weight.

The paraffin antifoulant is conventional, and any long-chain, saturated, hydrocarbon wax or oil may be used. Reactor loadings of the paraffin are from 0.01% to 0.3% by weight on the total monomer weight used.

After the reactor has been charged with deionized water, surfactant, and paraffin antifoulant, the reactor is either purged with nitrogen or evacuated to remove oxygen. The reactor is brought to temperature, and chain-transfer agent may optionally be added. The reactor is then pressurized with a mixture of vinylidene fluoride and hexafluoropropylene.

Chain-transfer agents which may be used are well-known in the polymerization of fluorinated monomers. Alcohols, carbonates, ketones, esters, and ethers are oxygenated compounds which serve as chain-transfer agents. Specific, but not limiting examples, are isopropyl alcohol, such as described in U.S. Pat. No. 4,360,652, acetone, such as described in U.S. Pat. No. 3,857,827, and ethyl acetate, as described in the Published Unexamined Application (Kokai) JP 58065711. Other classes of compounds which serve as chain-transfer agents in the polymerization of fluorinated monomers are halocarbons and hydrohalocarbons such as

chlorocarbons, hydrochlorocarbons,
chlorofluorocarbons, and hydrochlorofluorocarbons;
specific, but not limiting examples are
trichlorofluoromethane, such as described in U.S. Pat.
No. 4,569,978, and 1,1-dichloro-2,2,2-trifluoroethane.

5 Chain-transfer agents may be added all at once at the
beginning of the reaction, in portions throughout the
reaction, or continuously as the reaction progresses.
The amount of chain-transfer agent and mode of
addition which is used depends on the activity of the
10 agent and the desired molecular weight characteristics
of the product. The amount of chain-transfer agent
used is from 0.05% to 5% by weight on the total
monomer weight used, and preferably it is from 0.1 to
2% by weight.

15 The reactor is pressurized by adding vinylidene
fluoride and hexafluoropropylene monomers in a
definite ratio (first effective ratio) such that the
hexafluoropropylene ranges up to 48% of the combined
weight of the monomers initially charged. The first
20 effective ratio used will depend on the relative
reactivity of the two monomers at the polymerization
temperature chosen. The reactivity of vinylidene
fluoride and hexafluoropropylene has been reported in
Bonardelli et al., Polymer, vol. 27, 905-909 (June
25 1986). The relative reactivity is such that to obtain
a particular uniform copolymer composition, more
hexafluoropropylene has to be charged to the reactor
in the initial fill than will be incorporated into the
copolymer. At the convenient polymerization

temperature range of this invention, about twice as much hexafluoropropylene has to be charged to the reactor in the initial fill as will appear in the polymer.

5 The reaction can be started and maintained by the addition of any suitable initiator known for the polymerization of fluorinated monomers including inorganic peroxides, "redox" combinations of oxidizing and reducing agents, and organic peroxides. Examples of typical inorganic peroxides are the ammonium or
10 alkali metal salts of persulfates, which have useful activity in the 65°C to 105°C temperature range. "Redox" systems can operate at even lower temperatures and examples include combinations of oxidants such as hydrogen peroxide, t-butyl hydroperoxide, cumene
15 hydroperoxide, or persulfate, and reductants such as reduced metal salts, iron (II) salts being a particular example, optionally combined with activators such as sodium formaldehyde sulfoxylate or ascorbic acid. Among the organic peroxides which can
20 be used for the polymerization are the classes of dialkyl peroxides, peroxyesters, and peroxydicarbonates. Exemplary of dialkyl peroxides is di-t-butyl peroxide, of peroxyesters are t-butyl peroxy-pivalate and t-amyl peroxy-pivalate, and of
25 peroxydicarbonates are di(n-propyl) peroxydicarbonate, diisopropyl peroxydicarbonate, di(sec-butyl) peroxydicarbonate, and di(2-ethylhexyl) peroxydicarbonate. The use of diisopropyl peroxydicarbonate for vinylidene fluoride

polymerization and copolymerization with other fluorinated monomers is taught in U.S. Pat. No. 3,475,396, and its use in making vinylidene fluoride/hexafluoropropylene copolymers is further illustrated in U.S. Pat. No. 4,360,652. The use of di(n-propyl) peroxydicarbonate in vinylidene fluoride polymerizations is described in the Published Unexamined Application (Kokai) JP 58065711. The quantity of an initiator required for a polymerization is related to its activity and the temperature used for the polymerization. The total amount of initiator used is generally between 0.05% to 2.5% by weight on the total monomer weight used. Typically, sufficient initiator is added at the beginning to start the reaction and then additional initiator may be optionally added to maintain the polymerization at a convenient rate. The initiator may be added in pure form, in solution, in suspension, or in emulsion, depending upon the initiator chosen. As a particular example, peroxydicarbonates are conveniently added in the form of an aqueous emulsion.

As the reaction progresses, a mixture of vinylidene fluoride and hexafluoropropylene monomers is fed in a definite ratio (second effective ratio) so as to maintain reaction pressure. The second effective ratio used corresponds to the monomer unit ratio desired in the final composition of the copolymer, and it can range up to 24% of the combined weight of the monomers being fed continuously throughout the reaction. The feed of vinylidene

fluoride, hexafluoropropylene, and optionally initiator and chain-transfer agent is continued until the desired reactor fill is obtained.

Upon reaching the desired reactor fill, the monomer feeds are terminated. To achieve the

5 copolymer having optimum solution clarity and minimal extractables, all other feeds are stopped at the same time as the monomer feeds, and the reactor is vented as soon as is practicable. Alternatively, to achieve highest yield at the expense of solution clarity and
10 extractables, a react-out period to consume residual monomer is used with optional continuation of initiator feed. For react-out, the reaction temperature and agitation are maintained for a period of 20 to 30 minutes, but a longer period can be used
15 if required in order to consume monomer to the point where the reactor pressure is no longer falling to any significant degree. A settling period of typically 10 to 40 minutes may be used following the react-out period. During the settling period, temperature is
20 maintained but no initiator feed is used. The reactor is then cooled and vented.

The product is recovered as a latex. To obtain dry resin, the latex is coagulated, the coagulum is separated and the separated coagulum may be washed.

25 To provide powder, the coagulum is dried.

For the coagulation step, several well-known methods can be used including freezing, the addition of acids or salts, or mechanical shear with optional heating. The powder, if desired, can be further

processed into pellets or other convenient resin forms.

The following Examples further illustrate the best mode contemplated by the inventors for carrying out their invention and are to be construed as illustrative and not as in limitation thereof.

Melt viscosity measurements are by ASTM D3835 at 232°C and 100 s⁻¹.

Thermal properties are measured with a Differential Scanning Calorimeter (DSC) according to ASTM D3418.

HFP content was determined by ¹⁹F NMR according to the signal assignments and method described in Pianca et al., Polymer, vol. 28, 224-230 (Feb. 1987). A Unity 400 spectrometer at 376.3 MHz was used.

Spectra were obtained either in deuterated dimethyl formamide at 50° C with an excitation pulse width of 8.0 microseconds and a recycle delay of 10 seconds, in deuterated dimethyl sulfoxide at 80° C with an excitation pulse width of 6.0 microseconds and recycle delay of 5 seconds, or in deuterated acetone at 50° C with an excitation pulse width of 8.0 microseconds and a recycle delay of 20 seconds.

Molecular weights were measured by size exclusion chromatography (SEC). A Waters 150 C chromatographic device with a set of PL gel 2 mixed B columns with bead size of 10 microns was used at an operating temperature of 105 degrees C. HPLC grade dimethyl sulfoxide (DMSO) was used as the eluant at flow rate of 1.0 mL/min. The samples were prepared by

dissolution in DMSO for 5 hours at 100 degrees C, followed by filtration.

EXAMPLE 1

Into a 7.5 liter, stainless steel reactor were charged 4.799 kg of deionized water, 0.230 kg of a 1 wt% solution of a mixture of perfluoroalkanoate salts, and 0.004 kg of paraffin wax. The mixture was purged with nitrogen and agitated for 30 minutes. The reactor was sealed and heated to 80 degrees Celsius. The reactor was charged with 0.355 kg of vinylidene fluoride, 0.049 kg of hexafluoropropylene (a ratio of 88 vinylidene fluoride/12 hexafluoropropylene), and 0.120 kg of a 5 wt% solution of ethyl acetate in deionized water. The reaction conditions were stabilized at 80 degrees Celsius and 4480 kPa, and then the polymerization was begun by introducing 0.026 kg of an initiator emulsion consisting of 2 wt% di-n-propyl peroxydicarbonate and 0.15 wt% mixed perfluoroalkanoate salts dispersed in deionized water. The pressure rose to 4550 kPa with the addition of the initiator emulsion. The polymerization was maintained by the addition of the initiator emulsion at the rate of 0.112 kg per hour, and by the addition of a mixture of vinylidene fluoride/hexafluoropropylene in the ratio 95 vinylidene fluoride/5 hexafluoropropylene so as to maintain pressure. After 4.2 hours, totals of 1.890 kg of vinylidene fluoride and 0.140 kg of hexafluoropropylene had been charged to the reactor. All feeds were stopped, and the reactor was cooled. After 5 minutes of cooling, agitation speed was

reduced by 78% and surplus gases were vented. Agitation was stopped, the reactor was further cooled, and then it was emptied of latex. Polymer resin was isolated by coagulating the latex, washing the resulting solids with boiling water, and drying the solids at 110 degrees Celsius to yield fine powder. The resin so made had a melt viscosity of 2770 Pa.s, had a DSC melting point of 152 degrees Celsius, and had a hexafluoropropylene content as measured by NMR of 5.4 wt%.

10 EXAMPLE 2

Into a 7.5 liter, stainless steel reactor were charged 4.913 kg of deionized water, 0.230 kg of a 1 wt% solution of a mixture of perfluoroalkanoate salts, and 0.004 kg of paraffin wax. The mixture was purged with nitrogen and agitated for 30 minutes. The reactor was sealed and heated to 80 degrees Celsius. The reactor was charged with 0.415 kg of vinylidene fluoride, 0.215 kg of hexafluoropropylene (a ratio of 66 vinylidene fluoride/34 hexafluoropropylene), and 0.010 kg of ethyl acetate. The pressure was at 4895 kPa. The reaction conditions were stabilized at 80 degrees Celsius, and then the polymerization was begun by introducing 0.040 kg of an initiator emulsion consisting of 2 wt% di-n-propyl peroxydicarbonate and 0.15 wt% mixed perfluoroalkanoate salts dispersed in deionized water. The pressure dropped upon initiation and it was then maintained at 4825 kPa. The polymerization was maintained by the addition of the initiator emulsion at the rate of 0.176 kg per hour,

and by the addition of a mixture of vinylidene fluoride/hexafluoropropylene in the ratio 84 vinylidene fluoride/16 hexafluoropropylene so as to maintain pressure. After 2.2 hours, totals of 1.585 kg of vinylidene fluoride and 0.445 kg of hexafluoropropylene had been charged to the reactor. Monomer feeds were stopped, and residual monomer was consumed by maintaining the initiator emulsion feed and 80 degrees Celsius for 20 minutes. The initiator feed and agitation were stopped and the reactor was allowed to settle 10 minutes. The reactor was cooled to 45 degrees Celsius, vented, and then it was emptied of latex. Polymer resin was isolated by coagulating the latex, washing the resulting solids with boiling water, and drying the solids at 80 degrees Celsius to yield fine powder. The resin so made had a melt viscosity of 1220 Pa.s, had a DSC melting point of 114 degrees Celsius, and had a hexafluoropropylene content as measured by NMR of 17.2 wt.%.

EXAMPLE 3 (Comparative Example to Example 1)

Into a 7.5 liter, stainless steel reactor were charged 4.799 kg of deionized water, 0.230 kg of a 1 wt% solution of a mixture of perfluoroalkanoate salts, and 0.004 kg of paraffin wax. The mixture was purged with nitrogen and agitated for 30 minutes. The reactor was sealed and heated to 80 degrees Celsius. The reactor was charged with 0.400 kg of vinylidene fluoride, 0.030 kg of hexafluoropropylene (a ratio of 93 vinylidene fluoride/7 hexafluoropropylene), and 0.120 kg of a 5 wt.% solution of ethyl acetate in

deionized water. The reaction conditions were stabilized at 80 degrees Celsius and 4480 kPa, and then the polymerization was begun by introducing 0.026 kg of an initiator emulsion consisting of 2 wt% di-n-propyl peroxydicarbonate and 0.15 wt% mixed perfluoroalkanoate salts dispersed in deionized water. The polymerization was maintained by the addition of the initiator emulsion at the rate of 0.112 kg per hour, and by the addition of a mixture of vinylidene fluoride/hexafluoropropylene in the ratio 93 vinylidene fluoride/7 hexafluoropropylene so as to maintain pressure. After 3.1 hours, totals of 1.890 kg of vinylidene fluoride and 0.140 kg of hexafluoropropylene had been charged to the reactor. Monomer feeds were stopped, and residual monomer was consumed by maintaining the initiator emulsion feed and 80 degrees Celsius for 20 minutes. The initiator feed and agitation were stopped, and the reactor was allowed to settle for 10 minutes. The reactor was cooled to 45 degrees Celsius, vented, and then it was emptied of latex. Polymer resin was isolated by coagulating the latex, washing the resulting solids with boiling water, and drying the solids at 110 degrees Celsius to yield fine powder. The resin so made had a melt viscosity of 2550 Pa.s, had a DSC melting point of 154 degrees Celsius, and had a hexafluoropropylene content as measured by NMR of 6.0 wt.%.

EXAMPLE 4

Into a 293 liter stainless steel reactor were

charged 200.0 kg of deionized water, 1.00 kg of a 10 wt% solution of a mixture of perfluoroalkanoate salts, and 0.015 kg of paraffin oil. The reactor was evacuated and heated to a temperature of 91 degrees Celsius during the charging, and agitation was used.

5 To the reactor were added 12.6 kg of vinylidene fluoride, 0.8 kg of hexafluoropropylene (a ratio of 94 vinylidene fluoride/6 hexafluoropropylene), and 0.5 kg of ethyl acetate, which brought the reactor pressure to 4480 kPa. During the pressurization, when the
10 pressure reached 3445 kPa, a feed of initiator emulsion consisting of 2 wt% di-n-propyl peroxydicarbonate and 0.15 wt% mixed perfluoroalkanoate salts dispersed in deionized water was begun and was maintained at 9.0 kg/h until 4.6 kg
15 of initiator emulsion had been added. The rate of further initiator emulsion addition was adjusted so as to maintain a total monomer feed rate of 27.0 kg/h. A monomer mixture in the ratio 94 vinylidene fluoride/6 hexafluoropropylene was fed to the reactor so as to
20 maintain pressure at 4480 kPa until the totals of 85.3 kg of vinylidene fluoride and 5.4 kg of hexafluoropropylene had been charged to the reactor. All feeds were stopped, and residual monomer was consumed by maintaining 91° Celsius and agitation for
25 20 minutes and then by maintaining 91° Celsius for 35 minutes. The reactor was cooled, vented, and emptied of latex. Polymer resin was isolated by coagulating the latex, washing the resulting solids with water, and drying the solids to yield fine powder. The resin
30 so made had a melt viscosity of 1740 Pa.s, had a DSC

melting point of 155 degrees Celsius, and had a hexafluoropropylene content as measured by NMR of 4.7 wt. %.

EXAMPLES 5 to 12

- 5 Copolymers of examples 5 to 8 are made similarly to copolymers of Examples 1 or 2, and copolymers of examples 9 to 12 are made similarly to copolymers of Examples 3 or 4 and are shown in Table I.

TABLE I
EXPERIMENTAL EXAMPLES

	Example	1	2	5	6	7	8	3	4	9	10	11	12
5	(Detailed example which the example is similar too)	-	-	1	1	1	2	-	-	3	3	4	3
	Temperature, °C	80	80	80	80	80	80	80	91	80	80	91	80
	Pressure, kPa	4550	4825	4550	4480	4480	4480	4480	4480	4480	4515	4480	4480
10	Initial Fill [a]												
	Water, kg	4.799	4.913	4.837	4.768	4.797	4.723	4.799	200.0	4.837	4.768	200.0	4.723
	VDF, kg	0.355	0.415	0.365	0.365	0.460	0.400	0.400	12.6	0.390	0.365	11.0	0.455
	HFP, kg	0.049	0.215	0.030	0.129	0.163	0.207	0.030	0.8	0.017	0.060	1.9	0.128
	EtoAc Solution, kg	0.120	-	0.080	0.160	0.130	0.200	0.120	-	0.080	0.160	-	0.200
	EtoAc, kg	-	0.010	-	-	-	-	-	0.5	-	-	0.7	-
	NPP Emulsion, kg	0.026	0.040	0.026	0.033	0.036	0.040	0.026	4.6	0.026	0.033	3.7	0.040
15	Totals												
	VDF, kg	1.890	1.585	1.915	1.745	1.700	1.590	1.890	85.3	1.945	1.745	77.1	1.585
	HFP, kg	0.140	0.445	0.083	0.285	0.331	0.441	0.140	5.4	0.085	0.285	13.6	0.445
	NPP Emulsion, kg	0.506	0.460	0.413	0.422	0.352	0.463	0.405	8.5	0.540	0.491	8.3	0.563
	Melt Viscosity, Pa.s	2770	1220	3120	1660	1760	480	2550	1740	2240	1010	660	850
20	Melting Point, °C	152	114	156	132	125	116	154	155	159	141	139	126
	Polymer HFP, wt%	5.4	17.2	3.4	12.5	14.8	17.0	5.8	4.6	4.9	11.8	11.7	18.1

[a] Perfluoroalkanoate salt solution, perfluoroalkanoate salts, paraffin wax, and paraffin oil in examples 5 to 12 were the same as in the similar detailed examples.

The term "solution(s) having improved clarity and fluidity" as used in the specification and claims of this application means that the solution(s) of any particular copolymer of this invention having a particular nominal HFP content will provide solution(s) having descriptive properties analogous to those shown by Example 2 in Table II when dissolved in any of the solvents listed at the same concentration levels at which a copolymer having about the same particular nominal HFP content made by a typical process described in detail in the prior art provides solution descriptive properties analogous to those shown in Table II for Example 12.

**EVALUATION OF THE SOLUTION PROPERTIES OF THE
EXAMPLES**

The solution properties of examples 2 and 12 are shown in Table II. Mixtures of the indicated weight percent were prepared, using heat when necessary to dissolve the polymer completely and form a clear solution. Solutions were then allowed to cool and observed daily over a period of two weeks. The copolymer 2 showed a reduced tendency to gel and to be clearer than the copolymer 12. The retention of fluidity and clarity by the copolymer 2 is advantageous in applications which rely on polymer solutions, such as in the production of cast films and membranes.

The reduction in tendency toward gelation by the copolymers of the present invention is further

shown in Table II A. The gelation times of propylene carbonate solutions of some of the examples are shown in the table. A Rheometrics[®] dynamic stress rheometer DSR-200 was used to measure the gelation times of 20 wt% solutions of the polymers in propylene carbonate (the propylene carbonate was of nominal 99.7% purity). The rheometer was fitted with a Peltier fixture and solvent trap. A 40 mm parallel plate geometry was used with a gap of 1 mm. Solid copolymer was mixed with propylene carbonate at room temperature on the day of measurement, the container was sealed, and the solution was formed by heating and stirring the mixture in the sealed container for 1.0 hour in a Pierce Reacti-Therm[®] Heating/Stirring Module set at 120°C. The solutions were quickly loaded at the end of the dissolution period into the test fixture, which was preset at 100°C. A temperature cooling ramp in dynamic oscillatory mode at 1 Hz was begun as soon as the fixture temperature re-equilibrated at 100°C; re-equilibration typically required a minute or less. The cooling ramp was from 100°C to 15°C at a rate of 30°C/m. When 15°C was reached, a 1 minute equilibration time was used, and then a time sweep measurement was begun. The sample was held at 15°C during the time sweep measurement performed at 1 radian/s. The time sweep was continued until the gel point was reached. The gel point was taken as the point at which the solution storage modulus, G' , and the loss modulus, G'' , became equal. The gel time was taken as the time duration in the time

sweep to reach the gel point.

The relation between HFP content and the logarithm of the gelation time of the 20 wt% propylene-carbonate solutions is shown in Figure 3. It can be seen that the copolymers of the present invention have longer gelation times than the copolymers prepared according to the prior art over the whole range of HFP content. The reduced tendency toward gelation by the copolymers of the present invention is advantageous in processing such solutions for film casting and other solution applications.

TABLE II
SOLUTION PROPERTIES

	Polymer concentration and solvent	Appearance	
		Example 2	Example 12
5	10% in MEK	fluid, clear	fluid clear
10	20% in MEK clear	fluid, clear	by day 2, loose gel,
	30% in MEK	by day 14, some gel, clear	by day 1, loose gel, cloudy; by day 4, gel, cloudy
15	10% in MPK	fluid, clear	fluid, clear
	20% in MPK	fluid, clear	by hour 2, some gel, clear; by day 1, gel, slightly cloudy
20	10% in MiBK	fluid, clear	by day 4, gel, clear
	10% in CPO	fluid, clear	fluid, clear
	10% in CHO	fluid, clear	fluid, clear
	20% in CHO clear;	by day 2, some gel, clear	by day 1, some gel, by day 2, some gel,
25	cloudy		
30	10% in EtoAC clear	fluid, clear	by day 7, some gel,
	20% in EtoAC cloudy; gel,	fluid, clear	by day 1, fluid, by day 3, some cloudy
	10% in n-PrOAc	fluid, clear	fluid, clear
	10% in i-PrOAc clear	fluid, clear	by day 6, some gel,
35	10% in EGMEA	fluid, clear	by day 6, gel, clear
	10% in DMC clear	fluid, clear	by day 7, some gel,
	20% in DMC	fluid, clear	by day 1, some gel, cloudy; by day 2,
40	mostly		gel, cloudy
	20% in Blend 2 cloudy	fluid, clear	by day 14, fluid,

Notes for Table II

[a] Polymer concentrations are Wt% unless stated otherwise. MEK is methyl ethyl ketone, MPK is methyl propyl ketone, MiBK is methyl isobutyl ketone, CPO is cyclopentanone, CHO is cyclohexanone, 5 EtOAc is ethyl acetate, N-PrOAc is n-propyl acetate, i-PrOAc is isopropyl acetate, EGMEA is ethylene glycol monomethyl ether acetate, DMC is dimethyl carbonate, Blend 2 is composed of 35.4 parts MiBK, 29.8 parts CHO, and 30 parts DMC by weight.

TABLE II-A
SOLUTION GELATION TIME [a]

	<u>Example Number</u>	<u>Gelation Time</u>
5	1	425
	1	512
	3	342
	3	394
	6	4,913
10	6	8,322
	6	12,924
	10	934
	10	1,553
	10	3,191
15	2	77,000
	2	62,400
	12	14,100
	12	47,500

[a] 20 wt% solutions at 15°C in propylene carbonate. Gelation time is in seconds.

20 EVALUATION OF FILM GLOSS AND CLARITY

Some of the non-gelled solutions from the solution property tests were used to make films

which were tested for gloss and clarity. The films were cast on a Leneta Form 2A opacity chart using a 0.127 meter draw down applicator having a 250 micrometer gap. The cast films were dried for three days at room temperature. Film gloss was determined using a HunterLab Progloss PG-2 gloss meter, and the results are shown in Table III. Film haze was measured by determining the whiteness index (CIELAB L* value) of the film on the black portion of the opacity chart using a HunterLab Labscan 2 colorimeter, and the results are shown in Table IV. Films from copolymer 2 showed higher gloss from a wider range of solvents than films from copolymer 12. The haze in films from 2 and 12 was generally similar, but noticeably less haze was observed in films from 2 in several instances. The results, taken together, show that VDF/HFP copolymer of the present invention demonstrates an increased utility for high-gloss, high-transparency film applications.

TABLE III
GLOSS OF CAST FILMS

	Polymer concentration and solvent [a]	Gloss, 20 degree / 60 degree	
		Example 2	Example 12
5	20% in MEK	33.6 / 69.0	31.3 / 68.7
	10% in MPK	31.4 / 68.9	1.3 / 18.7
	10% in CPO	0.7 / 16.9	2.0 / 27.7
10	10% in EtOAc	29.4 / 66.6	29.4 / 68.0
	10% in n-PrOAc	31.9 / 70.1	16.0 / 57.0
	10% in i-PrOAc	31.6 / 69.4	15.4 / 56.2
	10% in DMC	35.4 / 70.6	30.1 / 68.6
15	20% in Blend 2	34.6 / 71.2	0.1 / 2.4

[a] Polymer concentration and solvent indicates the wt% and solvent the films were cast from. MEK is methyl ethyl ketone, MPK is methyl propyl ketone, CPO is cyclopentanone, EtOAc is ethyl acetate, n-PrOAc is n-propyl acetate, i-PrOAc is isopropyl acetate, DMC is dimethyl carbonate, Blend 2 is composed of 35.4 parts methyl isobutyl ketone, 29.8 parts cyclohexanone, and 30 parts DMC by weight.

TABLE IV
CLARITY OF CAST FILMS

	Polymer concentration and solvent [a]	Clarity, CIELAB L* [b]	
		Example 2	Example 12
5	20% in MEK	6.59	6.22
	10% in MPK	6.19	14.48
	10% in CPO	15.18	15.56
	10% in EtOAc	7.38	5.84
10	10% in n-PrOAc	5.64	7.34
	10% in i-PrOAc	5.61	7.79
	10% in DMC	6.21	5.73
	20% in Blend 2	5.36	17.85
15	[a] Polymer concentration and solvent indicates the wt% and solvent the films were cast from. MEK is methyl ethyl ketone, MPK is methyl propyl ketone, CPO is cyclopentanone, EtOAc is ethyl acetate, n-PrOAc is n-propyl acetate, i-PrOAc is isopropyl acetate, DMC is dimethyl carbonate, Blend 2 is composed of 35.4 parts methyl isobutyl ketone, 29.8 parts cyclohexanone, and 30 parts DMC by weight.		
20	[b] Guide to haze:		
	L* < 7	no haze	
25	7 < L* < 9	very slight haze	
	9 < L* < 11	slight haze	
	11 < L* < 15	moderate haze	
	15 < L*	severe haze	

EVALUATION OF THE THERMAL PROPERTIES OF THE EXAMPLES

The final melting point is an important parameter in the use and processing of semicrystalline polymers. It is known that the final melting point of VDF/HFP copolymers is related to the HFP content in the copolymers. The relation between HFP content and final melting point of the VDF/HFP copolymer examples is shown in Figure 1. The copolymers of the present invention and the copolymers prepared according to the prior art synthesis which details are available can be seen to fall on different melting point curves, indicating that they are different materials, with the prior art copolymers having a higher melting point at a given HFP content. The lower melting point property of the copolymers of the present invention can allow lower processing temperatures than for the prior art synthesis copolymers.

EVALUATION OF EXTRACTABLES IN DIMETHYL CARBONATE

General Procedure

1g of polymer and 9g of dimethyl carbonate were placed in a closed 25 ml container. The contents of the container were continually agitated by appropriate means while maintaining the desired temperature by appropriate means for 24 hours. The entire contents of the container were then transferred to a centrifuge tube and centrifuged to separate undissolved polymer. The liquid phase was transferred to a suitable tared container and the solvent evaporated. The residue in the container

was weighed and reported as percent by weight extractables.

5 The amount of polymer extracted into dimethyl carbonate at 40°C was measured. The data is shown in Table V. Copolymers prepared according to synthetic methods in the prior art for which details are available are labeled "N". Copolymers prepared according to the methods described for the present invention are labeled "U".

TABLE V

Effect of HFP Content, Molecular Number and
Uniformity of Compositional Distribution on Polymer
Dissolution in DMC

Sample Lot #	HFP (mole%)	Mw	Mn	Extractable (40°C) DMC	Composition
K2801	4.5	460000	145000	12.0%	N
K2801	4.5	495000	157000	10.5%	N
9521	2.1	427000	167000	3.11%	N
9527	3.6	473000	150000	14.30%	N
9529	2.8	417000	148000	9.29%	N
88	3.6	375000	138000	4.04%	U
90	2.3	483000	188000	0.23%	U
94	2.4	676000	240000	0.41%	U
96 (Ex1)	2.4	409000	159000	0.28%	U
98	2.4	351000	144000	1.11%	U
100 (Ex5)	1.5	523000	194000	0.41%	U
104	3.1	433000	157000	1.61%	U

A cursory examination shows that all N samples
have higher levels of polymer extracted into
dimethyl carbonate. Figure 2 shows a plot of the
extractables as a function of HFP content (mole%).
Two distinct curves are outlined for the two classes
of materials. The upper curve (N samples) shows
significantly higher levels of extractables for a
given level of HFP compared to the U curve.
Measured slopes for these curves are 3%
extractables/mole % HFP for the N polymers and 1.7%
extractables/mole % HFP for the U polymers.

The observed and calculated % extractables under both the single and dual functional model are shown for the N polymers in Table VI and for the U polymers in Table VII.

Table VI

5 Comparison of Wt. % Extractables of N polymer as a function of HFP content or HFP content and Mn

	% Extractable (meas)	% Extractable (calc model 1)	% Extractable (calc model 2)
	12.0%	12.6%	13.4%
10	10.5%	12.6%	10.1%
	3.11%	5.7%	3.2%
	14.30%	10.0%	10.5%
	9.29%	7.7%	9.7%

15 (Model 1) Wt % Extractable = 2.9 (HFP mole%) - 0.4
 (Model 2) Wt % Extractable = 46.4 + 1.7(HFP mole %) -
 0.00028 (Mn) .

Table VII

Comparison of Wt.% Extractables of -U polymer as a function of HFP content of HFP content of Mn

	% Extractable (meas)	% Extractable (calc model 1)	% Extractable (calc model 2)
5	4.04%	2.9%	3.1%
	0.23%	0.71%	0.75%
	0.41%	0.88%	0.48%
	0.28%	0.88%	1.1%
	1.11%	0.88%	1.2%
10	0.41%	-0.65%	-0.50%
	1.61%	2.1%	2.2%

(Model 1) % Extractable = $1.7(\text{HFP mole}\%) - 3.2$

(Model 2) % Extractable = $-1.2 + 1.5(\text{HFP mole}\%) - 8 \times 10^{-6}(\text{Mn})$.

In the specification and the attached claims,
the expression "having weight percent extractables
within 1.5% of the percent by weight extractables
calculated by an equation selected from the group
consisting of:

- a) $\text{Wt}\% \text{ Extractable} = 1.7(\text{HFP mole}\%) - 3.2$, and
b) $\text{Wt}\% \text{ Extractable} = -1.2 + 1.5(\text{HFP mole}\%) - 8 \times 10^{-6}(\text{Mn})$

means that the measured value of weight percent
extractables in dimethylcarbonate at 40°C must be
within 1.5 absolute percentage points from the
extractable value calculated for the particular
polymer by either equation.

That is, if the calculated value of %
extractables by either equation 1 or 2 is 3.0 and
the observed value is between 1.5 and 4.5% it falls

within the intended coverage value. Similarly if the observed value is 8.0% it will be within the intended coverage if the calculated value from either equation ranges from 6.5% to 9.5%.

5 In the above described procedure for determining extractables in dimethyl carbonate, centrifugation for thirty minutes at 1500 rpm at ambient temperature was employed to separate the solution from the insoluble matter and drying at 10 50 deg. C for 70 hours under mechanical pump vacuum was used to determine the weight of solids in the separated solution.



The subject matter which applicants regard as their invention is particularly pointed out and distinctly claimed as follows:

We claim:

1. A copolymer of vinylidene fluoride and hexafluoropropylene containing a maximum of about 24 weight percent hexafluoropropylene, having solutions of improved clarity and fluidity; for the copolymers having up to about 8 weight percent nominal HFP content, having weight percent extractables within plus or minus 1.5% of the percent by weight extractables calculated by an equation selected from the group consisting of:

a) $\text{Wt. \% Extractables} = 1.7(\text{HFP mole \%}) - 3.2$, and

b) $\text{Wt. \% Extractables} = -1.2 + 1.5(\text{HFP mole \%}) - 8 \times 10^{-6}(\text{Mn})$;

and for the copolymers having greater than about 8 weight percent nominal HFP content, having a DSC melting point at least 2.5°C lower than copolymers of the same nominal weight percent HFP content prepared by synthetic methods for which the prior art provides details.

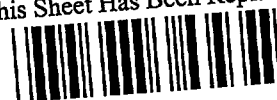
2. A solution of a copolymer as defined in claim 1 in a solvent having improved solution clarity and fluidity.

3. A copolymer as defined in claim 1 having greater than about 8 percent by weight HFP content.

4. A copolymer as defined in claim 1 having from about 2 to about 8 weight percent HFP content.

5. A copolymer as defined in claim 1 having from about 3 to about 6 weight percent HFP content.

6. A copolymer of vinylidene fluoride and





hexafluoropropylene prepared by the emulsion polymerization of vinylidene fluoride and hexafluoropropylene in a stirred aqueous reaction medium comprising:

- 5 (a) charging to a reactor: vinylidene fluoride and hexafluoropropylene in a first effective ratio, water, a water soluble surfactant capable of emulsifying both the initiator and the reaction mass during polymerization and an initiator to start polymerization;
 - 10 (b) feeding additional vinylidene fluoride and hexafluoropropylene in a second effective ratio to maintain reaction pressure until the desired reactor fill is obtained; and
 - 15 (c) obtaining vinylidene fluoride-hexafluoropropylene copolymer.
7. A process as defined in claim 6 wherein chain transfer agent to control molecular weight is included in the ingredients in the reaction.
8. A process as defined in claim 6 wherein
- 20 additional initiator is added during step (b) to aid in maintaining the reaction.
9. The vinylidene fluoride hexafluoropropylene polymer produced by claim 6.
- 25 10. A process as defined in claim 6 wherein hexafluoropropylene is present at up to 48% by weight of the first effective ratio.
11. A process as defined in claim 6 wherein hexafluoropropylene is present at up to 24% by weight of the second effective ratio and corresponds





to the comonomer ratio desired in the final vinylidene fluoride-hexafluoropropylene polymer product.

12. A vinylidene fluoride-hexafluoropropylene copolymer product having up to about 8 wt% hexafluoropropylene and having weight percent extractables within plus or minus 1.5% of the weight percent extractables calculated by either equation a) or b) defined in claim 1.

This Sheet Has Been Replaced

