

Fluoropolymer-containing powders

The present invention relates to a process for preparing fluoropolymer-containing powders, to powder prepared by the process, and, more particularly, fluoropolymer-containing powder suitable for use in powder coating. The invention also relates to a process for coating a substrate with a fluoropolymer-containing powder coating product, and to the resulting coated substrate.

Fluoropolymer-based coatings are extensively used as protective and decorative coatings because of their stability and durability when exposed to adverse weather conditions or to chemicals.

Solvent-based fluoropolymer coatings are well known in the art. They are prepared by dispersing the fluoropolymer in a suitable solvent, applying the dispersion to a substrate and subjecting the coated substrate to heat. The solvent used is generally an organic solvent which has no significant action on the fluoropolymer at ambient temperatures, but exhibits solvent activity at higher temperatures. Organic solvents are health hazards and environmentally damaging compounds and the recovery of these solvents is a costly and time-consuming procedure. Therefore, a need has arisen in the industry for cost-effective processes for preparing fluoropolymer-based coatings by

solventless processes.

Solventless processes for preparing pigmented poly(vinylidene fluoride)-based coatings have been proposed in British Patent Specification No. 2 194 539 A and U.S. Patent Specifications Nos. 4 770 939 and 5 030 394. These specifications indicate that, in previously proposed solventless processes for preparing pigmented poly(vinylidene fluoride) - based coatings, the mixture of powdered pigment and poly(vinylidene fluoride) was not satisfactory because the pigment was not perfectly wetted by the resin and the long term stability of coatings prepared from the mixture was adversely affected by the resulting empty spaces around the pigment particles. These specifications suggest that improvements in the previously proposed solventless processes can be obtained by including one or more compatible thermoplastic resins in the mixture of the poly(vinylidene fluoride) resin and the pigment.

In accordance with the above-mentioned specifications, a mixture of poly(vinylidene fluoride) resin, thermoplastic resin, and pigment is extruded and granulated and the resulting pellets are cooled to a very low temperature, for example -150°C , and ground cryogenically, cryogenic grinding being defined in those specifications as grinding at a temperature equal to or lower than about -50°C . Particles which are larger than a predetermined size are then sieved out.

One disadvantage of the process described in the above-mentioned specifications is the need for the cryogenic grinding of the pellets.

Cryogenic grinding of a material as described in the above-mentioned specifications requires the use of large amounts of a cooling medium, such as liquid nitrogen, to cool and embrittle the material before grinding, to cool the mill to very low temperatures, and to maintain the mill at a temperature of no higher than -50°C during grinding. Cryogenic grinding is, therefore, an intrinsically expensive technique because of the large amounts of coolant required and the need for specially designed grinding mills which can withstand continuous operation under the extremely low temperatures used in cryogenic grinding. It is, however, necessary for many materials to be ground cryogenically because they can only be ground satisfactorily if they are cooled to below the embrittlement temperature by being brought to very low temperatures.

A process for preparing fluoropolymer-containing powders in which the necessity for grinding at very low temperatures, for example, temperatures below -50°C , can be avoided would thus represent an important contribution to the art. Powders with improved properties would also represent an important contribution to the art.

The present invention provides a process for preparing a fluoropolymer-containing powder, which

comprises mixing a thermoplastic fluoropolymer with at least one other thermoplastic polymer which, in the proportions used, is compatible with the fluoropolymer in the melt, obtaining from the mixture a particulate solid mass in which the fluoropolymer has a degree of crystallinity (as hereinafter defined) of at least 85 %, and grinding the particulate solid mass.

As discussed in greater detail later in this specification, the particulate solid mass will typically be in the form of, for example, granules or pellets, but the size of the particles is not critical provided that the particulate solid mass is suitable for grinding.

The fluoropolymer (or fluorine-containing polymer) is advantageously a fluorohydrocarbon homo- or copolymer, for example, a copolymer comprising at least 80 mass %, preferably at least 90 mass %, of units derivable from vinylidene fluoride and up to 20 mass %, preferably up to 10 mass %, of units derivable from at least one other fluorine-containing monomer. Suitable fluorine-containing comonomers which may be used with vinylidene fluoride include tetrafluoroethylene, hexafluoropropene and vinyl fluoride. If a comonomer is used, the comonomer is preferably such that the crystallinity of the copolymer is not significantly less than that of the pure homopolymer, for example, the pure poly(vinylidene fluoride). The fluoropolymer is preferably poly(vinylidene fluoride).

The fluoropolymer advantageously has a weight average molecular weight (determined by gel permeation chromatography using polyethylene glycol/polyethylene oxide standards) in the range of from 20,000 to 200,000, a melting temperature in the range of from 160°C to 180°C, preferably 160°C to 170°C, a melt flow index (according to ASTM D1238) in the range of from 10 to 50 g/10 min, and a melt viscosity (according to ASTM D3835) in the range of from 6000 to 12000 P (600 to 1200 Pas) at 230°C.

The fluoropolymer is mixed with at least one other thermoplastic polymer which, in the proportions used, is compatible with the fluoropolymer in the melt. The fluoropolymer is itself thermoplastic, but, for convenience, the term "thermoplastic polymer" is used herein, unless the context requires otherwise, to mean a thermoplastic polymer other than the fluoropolymer. Although the possibility of the other thermoplastic polymer itself being a fluoropolymer is not ruled out, the other thermoplastic polymer is preferably not a fluoropolymer.

Preferred thermoplastic polymers are acrylic polymers with units derived from acrylates and/or methacrylates. Examples of suitable copolymers are those comprising units derivable from an alkyl (meth)acrylate, preferably methyl methacrylate, and units derivable from at least one other olefinically unsaturated monomer. Such other olefinically unsaturated monomers are

preferably also alkyl acrylates or alkyl methacrylates, for example, ethyl acrylate, butyl methacrylate or isobutyl methacrylate. Acrylic acid and methacrylic acid are also suitable as the other olefinically unsaturated monomer. Advantageously, the copolymers comprise at least 75 mass % of units derivable from an alkyl (meth)acrylate and up to 25 mass % of units derivable from one or more other olefinically unsaturated monomers. The thermoplastic polymer is preferably poly(methyl methacrylate) or an alkyl methacrylate/alkyl acrylate copolymer.

The thermoplastic polymers preferably have a weight average molecular weight (determined by gel permeation chromatography using polyethylene glycol/polyethylene oxide standards) in the range of from 20,000 to 200,000, a viscosity in the range of from 7 to 17 P (0.7 to 1.7 Pas) in a 40 % solution in a 95:5 by mass mixture of toluene and ethylene glycol methyl ether.

The mass ratio of the fluoropolymer to the thermoplastic polymer is advantageously in the range of from 80:20 to 40:60. For commercial reasons, a mass ratio in the range of from 75:25 to 65:35 is normally preferred, but it is an advantage of the invention that decreasing the proportion of fluoropolymer does not in general make grinding more difficult: in fact grinding may well be easier. The above-mentioned British and U.S. specifications, on the other hand, indicate that

compositions containing lower amounts of poly(vinylidene fluoride) have to be ground at "lower temperatures", that is, they are more difficult to grind.

The mixture of the fluoropolymer and the thermoplastic polymer may optionally contain other additives. Examples of additives which may be included are pigments and wet flow promoting agents.

The mixture preferably contains at least one pigment, and the use of a pigment will normally be essential when the powder is to be used for coating a substrate which will in use be exposed to ultraviolet radiation. The amount of pigment used varies with the choice of pigment. For example, for a white coating which comprises titanium dioxide, 20 to 40 mass % of titanium dioxide, based on the mass of the mixture, including the titanium dioxide, may be required.

The mixture optionally contains at least one flow-promoting agent. (Flow-promoting agents, or flow aids, are well known in the art, and are typically acrylic polymers of very low molecular weight.) We have surprisingly found, however, that the invention may in some cases, particularly when amounts of pigment are relatively low, make it possible to obtain a powder coating material which has good flow characteristics even in the absence of a flow-promoting agent. For the purposes of the present invention, therefore, a flow-promoting agent is not essential.

The fluoropolymer and the thermoplastic polymer are blended, preferably in the melt, a suitable blending temperature for mixtures of poly(vinylidene fluoride) and poly(methyl methacrylate) being in the range of from 190 to 240°C. Other additives, for example, pigment, required in the final powder may be incorporated into the mixture before or during melt-blending, or, in some cases (for example, in the case of a dry flow aid), may be incorporated during grinding. Blending may be carried out, for example, in an extruder, normally after pre-mixing of the components of the blend. When blending, the temperature of the blending apparatus may, if desired, be set to a temperature above the crystalline melting point of a fluoropolymer. In another blending method, the blending apparatus may be set to a temperature below the crystalline melting point of the fluoropolymer and additional energy may be supplied to the mixture by, for example, shear.

A particulate solid mass is obtained from the mixture of the fluoropolymer and the thermoplastic polymer. We have surprisingly found that the necessity for grinding of the particulate solid mass at temperatures below -50°C can be avoided, while obtaining a satisfactory product, when the fluoropolymer in the particulate solid mass is in a highly crystalline form, that is, when it has a degree of crystallinity (as hereinafter defined) of at least 85%, advantageously at

least 90 %, and preferably at least 95 %.

For the purposes of this specification, the degree of crystallinity of the fluoropolymer in the particulate solid mass to be fed to the grinding step is arrived at by dividing the heat of fusion (ΔH_f) of a sample of the particulate solid mass (including any additives, for example, pigments and flow improvers) by the heat of fusion of a sample of the pure fluoropolymer which has been brought to its crystalline melting temperature and has been cooled, or allowed to cool, to 20°C (in still air at 20°C) in the form of a block having dimensions 170 mm x 73 mm x 25 mm, and adjusting the resulting value to allow for the proportion of the fluoropolymer in the particulate solid mass. The heat of fusion in each case is measured by Differential Scanning Calorimetry (DSC), using a heating rate of 10°C/min.

Thus the degree of crystallinity of the fluoropolymer in the particulate solid mass is defined herein as:

ΔH_f (particulate solid mass)	x	100
ΔH_f (pure fluoropolymer melted and cooled under the conditions defined above)		proportion by mass of that fluoropolymer in the particulate solid mass

If the particulate solid mass contains more than one fluoropolymer, the fluoropolymer to be used in the pure form as the reference for the purposes of the above

definition is the fluoropolymer present in the greater, or greatest, proportion by mass, and the proportion of that fluoropolymer should be used in the above calculation. If the DSC trace for the sample of the particulate solid mass has more than one melting peak (indicating the presence in the particulate solid mass of crystalline constituents of significantly different melting points) the heat of fusion is calculated, for the purposes of the above definition, using the melting peak corresponding to the melting range closest to that of the pure fluoropolymer used as the reference.

A solid mass in which the fluoropolymer is in a highly crystalline form is advantageously obtained from a mixture in which the fluoropolymer is above its crystalline melting point, preferably a molten mixture, by ensuring that cooling of the mixture to ambient temperature from the temperature at which crystallization of the fluoropolymer commences takes place relatively slowly (as compared with the rapid cooling obtained by quenching). Advantageously, the mixture is allowed to cool in substantially still air at ambient temperature. Accordingly, the invention also provides a process for preparing a fluoropolymer-containing powder, which comprises preparing a molten mixture of a fluoropolymer and at least one thermoplastic polymer which, in the proportions used, is compatible with the fluoropolymer in the melt, obtaining a particulate solid mass from the

molten mixture by a process which includes the step of causing or allowing the molten mixture to cool, preferably to ambient temperature, without quenching, and, if necessary, breaking up the solid material obtained in the cooling step, and grinding the particulate solid mass.

In one preferred embodiment of the invention, the fluoropolymer and the thermoplastic polymer are blended, preferably melt-blended, in an extruder (after pre-mixing), and the mixture is extruded to give flat blocks which are then allowed to cool in air at ambient temperature, without the use of forced cooling. The size of the blocks is not critical, and will be dictated largely by handling considerations, although if very large blocks are used an undesirably long time may be required for complete cooling of the blocks. Block sizes of the order of 200 mm x 100 mm x 50 mm have been found to be convenient, but blocks significantly larger or smaller than this could be used if desired.

Other methods by which a solid mass may be obtained from a molten mixture of the fluoropolymer and the thermoplastic polymer include quenching the mixture to give a solid product in, for example, sheet or tape form, and then subjecting the solid product to an annealing or orientation step.

The molten mixture may be quenched by any suitable method, for example, by passing it into a bath of liquid

and/or by spraying it with a liquid.

The quenched extrudate may then be annealed, for example, at a temperature of up to 160°C, preferably from 60 to 140°C, most preferably from 100 to 140°C, until the desired degree of crystallinity is obtained.

Orientation of a solid product in, for example, sheet or ribbon form, may be carried out using two rollers, the second of which has a higher peripheral speed than the first.

As indicated earlier, the size of the particles in a particulate solid mass used in accordance with the invention is not critical, provided that the particulate solid mass is suitable for grinding. For convenience, the particulate solid mass will typically be in the form of, for example, granules or pellets, but larger particles may be employed where the form of the grinder permits.

The solid product obtained from the cooling step may in some cases be obtained directly in the form of particles of a suitable size for feeding to the grinder. In this case, no further breaking up of the particles is required before grinding. Normally, however, breaking up of the cooled solid mass will be necessary in order to produce the particulate solid mass to be fed to the grinder. Such breaking up may be effected by any suitable means, for example, by crushing and/or shearing.

The term "grinding" used in this specification includes all size-reduction processes suitable for producing a powder from a particulate solid mass, and is not restricted to, for example, processes in which material is treated by opposed surfaces. Grinding may be effected by any suitable means.

In a preferred embodiment of the invention, the particulate solid mass is ground in a pin-disc mill, also known as a stud mill or needle mill. The material used in the above-mentioned British and U.S. specifications did not give a satisfactory product when ground using a needle mill, even when cryogenic grinding was used (see Comparative Example B in the said British and U.S. specifications).

In a further embodiment, the particulate solid mass is ground in a hammer mill.

In a further embodiment, which is not at present preferred, the particulate solid mass is ground in a jet mill in which size reduction is effected by the high-speed collision of particles in a fluidised bed.

In accordance with the invention, grinding of the particulate solid mass at the very low temperatures required in the above-mentioned British and U.S. specifications is not necessary, as the particulate solid mass is inherently sufficiently brittle to make it possible to obtain a satisfactory product by grinding at higher temperatures. Thus, grinding may, if desired, be

carried out in a mill that not specially designed for use at very low temperatures. Some cooling of the mill, e.g., by the circulation of cooled air or water, or by the use of a trickle of a small amount of liquid nitrogen, may be desirable to remove the heat which is inevitably generated during grinding, but the use of the very large amounts of liquid nitrogen required for cryogenic grinding is unnecessary. The particulate solid mass obtained in accordance with the invention can of course be subjected to grinding at very low temperatures if desired, but in general grinding at very low temperatures is avoided when it is possible to do so.

Grinding temperatures are advantageously higher than -50°C , preferably not lower than -35°C , and most preferably not lower than -20°C . In some cases it may be desirable that the grinding temperature should not be higher than 0°C . The air temperature at the outlet of the mill advantageously does not exceed $+50^{\circ}\text{C}$, and is preferably in the range of from 0°C to $+50^{\circ}\text{C}$.

The present invention more especially provides a process for preparing a fluoropolymer-containing powder suitable for use in a powder coating process which comprises preparing a molten mixture of a fluoropolymer and at least one thermoplastic polymer which, in the proportions used, is compatible with the fluoropolymer in the melt, extruding the mixture, obtaining from the extrudate a particulate solid mass in which the

fluoropolymer has a degree of crystallinity (as hereinbefore defined) of at least 85 %, advantageously at least 90 %, and preferably at least 95 %, and grinding the particulate solid mass at a temperature of higher than -50°C , preferably not lower than -35°C , and especially not lower than -20°C . Advantageously, the air temperature at the outlet of the mill is in the range of from 0 to $+50^{\circ}\text{C}$.

After the grinding step, the resulting powder may, if desired or required, be sieved to remove particles having a particle size greater than a particular value. If, for example, a powder coating product is required, particles having a particle size greater than about $120\text{ }\mu\text{m}$ are preferably removed. The particle size desired will depend on the application, but typically a powder coating product will have no, or only a small percentage of, particles with a size of less than 10 microns, with a majority of the particles having a size of more than 32 microns. Advantageously a majority of the particles have a particle size of less than 90 microns.

A powder obtained by the process of the present invention may be applied to a substrate using any suitable means, e.g., using electrostatic spray apparatus, a cloud chamber, a fluidised bed, or triboelectric coating apparatus.

The powder may be applied directly onto the substrate. Advantageously however, the powder is applied

over one or more intermediate layers. Preferably, a primer, for example, a primer comprising an epoxy resin, is used as an intermediate layer.

After application to the substrate the powder is subjected to a heat treatment to form a coherent coating layer. The heat treatment is preferably carried out at a temperature in the range of from 180 to 260°C, more preferably 200 to 240°C.

We have found that powder coating products obtained in accordance with the invention, in which the fluoropolymer is present in a highly crystalline form, have a sharper melting point and better flow and levelling characteristics than previously proposed poly(vinylidene fluoride) powder coating products such as those obtained in accordance with the teaching of the above-numbered British and U.S. specifications, and the coated substrate has an improved appearance, for example, they showed less "orange-peel effect."

The following Example illustrates the invention.

A commercially available sample of poly(vinylidene fluoride) resin sold under the trade mark KYNAR 710 and having a weight average molecular weight of about 84,000 (determined by gel permeation chromatography using dimethylformamide as the solvent and using polyethylene glycol/polyethylene oxide standards), was heated to a temperature of 220°C and allowed to cool to 20°C in still

air at 20°C in the form of a block having dimensions 170 mm x 73 mm x 25 mm. The heat of fusion of the material obtained was measured by DSC using a heating rate of 10°C/min and was found to be 60 J/g.

A mixture comprising 63 mass % of the above-identified poly(vinylidene fluoride) resin, 26 mass % of a methyl methacrylate/ethyl acrylate copolymer having a weight average molecular weight of about 51,000 (determined as above), 1 % of Resiflow flow enhancing agent and 10 % of pigment was melt-blended in a twin screw extruder, after pre-mixing, under the following conditions: 200 rpm; torque 50 to 60 %; set temperatures 175 to 200°C. Resiflow is a low molecular weight acrylic polymer, and is a standard flow aid. "Resiflow" is a trade mark. The molten mixture was extruded, the extrudate was quenched in a water bath, and the quenched material was pelletised to give pellets approximately 4 mm in length and 2 mm in diameter. The heat of fusion of the quenched material was 28.6 J/g, and the degree of crystallinity of the polyvinylidene fluoride in the pellets, measured by the method described herein, was thus 75.6 %

A sample of the pellets was cryogenically ground in an Alpine 160 UPZ cryogenic mill fitted with a fan beater system. "Alpine" is a trade mark. A 0.3 mm screen was used. The temperature of the pellets at the inlet of the mill was -100°C, while the temperature at the outlet was lower than -50°C. The _____

powder obtained was sieved to remove particles having a size greater than 120 μm .

A further sample of the pellets was heated to 200°C to remelt the polymeric materials, and the molten mixture was extruded to form blocks which were allowed to cool overnight in air at ambient temperature (about 20°C), and then broken up, using a granulator, to give a particulate solid mass having a particle size of 3 to 10 mm. The particulate solid mass had a heat of fusion of 36.5 J/g, and the fluoropolymer therefore had a degree of crystallinity of 96.6 %.

Samples of the slow-cooled particulate solid mass were ground using a pin disc mill. When grinding the first of these samples, liquid nitrogen was trickled through the mill at a slow rate to remove the heat generated during grinding, the amount of liquid nitrogen required being very much less than that required for cryogenic grinding. The flow rate was adjusted so that the air temperature at the outlet of the mill was 15°C. A second sample was ground without the use of liquid nitrogen, and in this case the air temperature at the outlet of the mill was 13 - 29°C, the temperature rising as grinding progressed. In each case the powder obtained by grinding was sieved to remove particles larger than 120 μm .

The particle size distribution of the powders was as follows:

<u>Material</u>	<u>Particle size Distribution</u>
Quench-cooled	100 % > 10 μm 92 % > 32 μm 17 % > 80 μm
Slow-cooled (Chilled mill grinding)	98 % > 10 μm 86 % > 32 μm 25 % > 80 μm
Slow-cooled (No liquid nitrogen used during grinding)	98 % > 10 μm 88 % > 32 μm 22 % > 80 μm

Materials with a particle size distribution broadly comparable to that of quenched-cooled material were thus obtained without the need for cryogenic grinding.

Each of the three powders obtained as described above was electrostatically sprayed onto an untreated aluminium panel and heated to 240°C for 10 minutes. A continuous film of thickness 60 to 70 μm was obtained in each case. Visual inspection of the coated panels during the heating step indicated that the slow-cooled materials flowed better than the quench-cooled material, and the final films obtained from the slow-cooled materials showed less "orange peel" effect than did the final films from the quench-cooled material.

CLAIMS:

1. A process for preparing a fluoropolymer-containing powder, which comprises mixing a thermoplastic fluoropolymer with at least one other thermoplastic polymer which, in the proportions used, is compatible with the fluoropolymer in the melt, obtaining from the mixture a particulate solid mass in which the fluoropolymer has a degree of crystallinity (as hereinbefore defined) of at least 85 %, and grinding the particulate solid mass.

2. A process as claimed in claim 1, wherein the said degree of crystallinity is at least 90 %.

3. A process as claimed in claim 1, wherein the said degree of crystallinity is at least 95 %.

4. A process for preparing a fluoropolymer-containing powder, which comprises preparing a molten mixture of a thermoplastic fluoropolymer and at least one other thermoplastic polymer which, in the proportions used, is compatible with the fluoropolymer in the melt, obtaining a particulate solid mass from the molten mixture by a process which includes the step of causing or allowing the molten mixture to cool without quenching, and, if necessary, breaking up the solid material obtained in the cooling step, and grinding the particulate solid mass.

5. A process as claimed in any one of claims 1 to 4, wherein the fluoropolymer is a copolymer



comprising at least 80 mass % of units derivable from vinylidene fluoride and up to 20 mass % of units derivable from at least one other fluorine-containing monomer.

6. A process as claimed in claim 5, wherein the other fluorine-containing monomer is selected from tetrafluoroethylene, hexafluoropropene and vinyl fluoride.

7. A process as claimed in any one of claims 1 to 4, wherein the fluoropolymer is poly(vinylidene fluoride).

8. A process as claimed in any one of claims 1 to 7, wherein the other thermoplastic polymer is a polymer other than a fluoropolymer.

9. A process as claimed in any one of claims 1 to 8, wherein the other thermoplastic polymer is a polymer comprising units derivable from an acrylate or methacrylate.

10. A process as claimed in any one of claims 1 to 9, wherein the other thermoplastic polymer is a copolymer comprising at least 75 mass % of units derivable from an alkyl(meth)acrylate and up to 25 mass % of units derivable from at least one other olefinically unsaturated monomer.

11. A process as claimed in any one of claims 1 to 9, wherein the other thermoplastic polymer is poly(methyl methacrylate) or an alkyl methacrylate/alkyl



acrylate copolymer.

12. A process as claimed in any one of claims 1 to 11, wherein the mass ratio of the fluoropolymer to the other thermoplastic polymer is in the range of from 80:20 to 40:60.

13. A process as claimed in any one of claims 1 to 4, wherein the fluoropolymer is poly(vinylidene fluoride) and the other thermoplastic polymer is poly(methyl methacrylate) or an alkyl methacrylate/alkyl acrylate copolymer and wherein the mass ratio of poly(vinylidene fluoride) to the other thermoplastic polymer is in the range of from 75:25 to 65:35.

14. A process as claimed in any one of claims 1 to 13, wherein the mixture of the fluoropolymer and the other thermoplastic polymer also comprises a pigment.

15. A process as claimed in any one of claims 1 to 14, wherein the mixture of the fluoropolymer and the other thermoplastic polymer also comprises a flow promoting agent.

16. A process as claimed in claim 1 or any claim dependent thereon, wherein the fluoropolymer and the other thermoplastic polymer are blended in the melt to form a molten mixture and the molten mixture is cooled, or allowed to cool, without quenching.

17. A process as claimed in any one of claims 1 to 16, wherein the fluoropolymer and the other thermoplastic polymer are blended in the melt and the



molten mixture is allowed to cool in air at ambient temperature.

18. A process as claimed in any one of claims 1 to 3 and claims 5 to 15 so far as they are dependent on claim 1, wherein the fluoropolymer and the other thermoplastic polymer are blended in the melt and the molten mixture is quenched to give a solid product which is then subjected to an annealing or orientation step.

19. A process as claimed in claim 18, wherein the annealing step is carried out at a temperature in the range of from 60 to 140°C.

20. A process as claimed in any one of claims 1 to 19, wherein the particulate solid mass is ground in a pin disc mill.

21. A process as claimed in any one of claims 1 to 20, wherein the particulate solid mass is ground at a temperature higher than -50°C.

22. A process as claimed in claim 21, wherein the grinding temperature is not lower than -35°C.

23. A process as claimed in claim 21 or 22, wherein the particulate solid mass is ground at such a temperature that the air temperature at the outlet of the mill is in the range of from 0°C to +50°C.

24. A process for preparing a fluoropolymer-containing powder suitable for use in a powder coating process, which comprises obtaining a molten mixture of a thermoplastic fluoropolymer and at least one other thermoplastic polymer which, in the proportions used, is



compatible with the fluoropolymer in the melt, extruding the mixture, obtaining from the extrudate a particulate solid mass in which the fluoropolymer has a degree of crystallinity (as hereinbefore defined) of at least 85 % and grinding the particulate solid mass at a temperature of higher than -50°C .

25. A process as claimed in claim 24, wherein the product of the grinding step is sieved to remove particles having a particle size greater than about $120\text{ }\mu\text{m}$.

26. A fluoropolymer-containing powder obtained by a process as claimed in any one of claims 1 to 25.

27. A process for coating a substrate which comprises applying a fluoropolymer-containing powder as claimed in claim 26 to the substrate and heating the coated substrate.

28. A process as claimed in claim 27, wherein the fluoropolymer-containing powder is applied over a primer layer.

29. A coated substrate obtained by a process as claimed in claim 27 or claim 28.

30. The use in powder coating of a powder comprising a thermoplastic fluoropolymer and at least one other thermoplastic polymer which, in the proportions used, is compatible with the fluoropolymer in the melt, the fluoropolymer having a degree of crystallinity (as hereinbefore defined) of at least 85 %.

