

TITLECOATING OF LIQUID CRYSTALLINE POLYMERS WITH FLUORO-
POLYMERS

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FIELD OF THE INVENTION

Ovenware made of liquid crystalline polymer (LCP) may be coated with a fluoropolymer to obtain an LCP ovenware part with a so-called non-stick surface.

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TECHNICAL BACKGROUND

Thermotropic (melt processible) liquid crystalline polymers (LCPs) are noted for many good properties, including good melt processability, high temperature resistance, good chemical resistance, and good flame resistance. This and other properties makes them especially useful for ovenware and other uses where some or all of these properties are valuable. However, like many other materials which are used for cooking and other uses, the food or other materials may stain and/or stick to the LCP surface. As is well known to those who cook, it is common to coat surfaces that come into contact with food, especially during cooking and/or heating, with a material to which the food does not stick, such as a fluoropolymer.

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Since fluoropolymers don't stick well to other materials it is often necessary to treat the substrate surface in order to improve adhesion of the fluoropolymer layer, sometimes done by surface treatment of the substrate and/or the use of primers. To those skilled in the art of LCPs this would seem even more difficult, since LCPs are relatively chemically stable, and are notorious for not sticking well to other substances. It has been found that LCPs may be coated with fluoro-

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polymers to obtain adhesion good enough for use in ovenware and for other uses, even if the LCP is not completely coated (encapsulated) and/or involving large surface areas, but only coated on one or more surfaces.

5 Japanese Patent Application 3-95954 describes the coating of an LCP wafer carrier with a fluoropolymer. No mention is made of coating only a single surface or surface treatment of the LCP before coating.

SUMMARY OF THE INVENTION

10 This invention concerns a part made of thermotropic liquid crystalline polymer and coated with a fluoropolymer coating. Preferably this part is an ovenware part.

DETAILS OF THE INVENTION

15 Herein certain terms are used and are defined below:

• A "fluoropolymer" is a synthetic polymer containing fluorine bound directly to carbon. Preferably the fluoropolymer contains at least about 25 weight percent fluorine, more preferably at least about 40 weight percent fluorine, and especially preferably at least about 50 weight percent fluorine. One type of preferred fluoropolymer is a perfluoro fluoropolymer.

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• A (thermotropic) "liquid crystalline polymer" is a polymer which is anisotropic when tested by the "TOT" test as described in U.S. Patent 4,118,372. Preferred LCPs are polyesters and poly(ester-amides), and polyesters are more preferred.

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Any thermotropic LCP may be used in this process. Suitable thermotropic LCPs, for example, are described in U.S. Patents 3,991,013, 3,991,014 4,011,199, 4,048,148, 4,075,262, 4,083,829, 4,118,372, 4,122,070, 4,130,545, 4,153,779, 4,159,365, 4,161,470, 4,169,933, 4,184,996, 4,189,549, 4,219,461, 4,232,143, 4,232,144, 4,245,082,

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4,256,624, 4,269,965, 4,272,625, 4,370,466, 4,383,105,
4,447,592, 4,522,974, 4,617,369, 4,664,972, 4,684,712,
4,727,129, 4,727,131, 4,728,714, 4,749,769, 4,762,907,
4,778,927, 4,816,555, 4,849,499, 4,851,496, 4,851,497,
5 4,857,626, 4,864,013, 4,868,278, 4,882,410, 4,923,947,
4,999,416, 5,015,721, 5,015,722, 5,025,082, 5,086,158,
5,102,935, 5,110,896, and 5,143,956, and European Patent
Application 356,226. Useful thermotropic LCPs include
polyesters, poly(ester-amides), poly(ester-imides), and
10 polyazomethines. Preferred thermotropic LCPs are polyes-
ters or poly(ester-amides), and it is especially pre-
ferred that the polyester or poly(ester-amide) is partly
or fully aromatic. By aromatic is meant aromatic group
form the main chain (backbone) of the LCP, along with any
15 functional groups (such as ethers, esters and amides)
needed to connect the aromatic groups, and that aliphatic
groups may be attached to the aromatic rings, such as the
repeat unit derived from t-butylhydroquinone.

In many instances it is preferred that the LCP used
20 have a relatively high melting point, preferably above
about 300°C, more preferably above about 325°C, even more
preferably above about 350°C, and even more preferably
above about 400°C, when measured by differential scanning
calorimetry at a heating rate of 10°C/min, and wherein the
25 peak of the melting endotherm on a second heating cycle
is taken as the melting point.

The fluoropolymer may be applied in any way. For
example it could be a film which is laminated with heat
and pressure onto the LCP surface. Preferably it is a
30 particulate material which is either a powder, or a pow-
der suspended (for example in an emulsion or dispersion)
in a liquid such as water, which is applied to the LCP
surface to be coated, as by spraying (electrostatic

spraying in the case of a powder), with a doctor knife, or other applicable method. After the liquid carrier (if present) is removed, usually by volatilization, the coating is baked until it forms a coherent film, which preferably adheres to the substrate, in this case the treated LCP surface. For fluoropolymers which contain relatively high amounts of fluorine, this bake temperature is often relatively high, $>300^{\circ}\text{C}$ for a substantial amount of time, for example 10-60 minutes. Therefore when using such coatings it is preferable that the LCP have a relatively high melting point so that the LCP part being coated does not change its shape and/or dimensions.

Such fluoropolymer coatings are known in the art, see for instance C. P. Izzo in Handbook of Plastics, Elastomers and Composites, 3rd Ed., C.A. Harper, Ed., McGraw Hill, New York, 1996, Chapter 6, and sometimes contain other materials which help produce smooth, uniform and adherent coatings. These other materials may include one or more of fillers, pigments, one or more other polymers, or other materials. The fluoropolymer coating preferably contains at least 10 percent by weight of fluoropolymer, more preferably at least about 25 percent by weight of fluoropolymer, and especially preferably at least about 50 percent by weight of fluoropolymer. These fluoropolymer coating materials and any associated needed materials such as primers are available commercially, as from E. I. DuPont de Nemours & Co., Inc., Wilmington, DE U.S.A. They may be powder coatings or dispersion (dispersed in water and/or a solvent) coatings. They may also contain more than one type of fluoropolymer. For example a useful coating material is Teflon® FEP Resin Finish Clear, Product Code #856-200,

available from E. I DuPont de Nemours & Co., Inc., Wilmington, DE U.S.A.

The coated LCP articles are useful in any application where the surface properties of the fluoropolymer are valued, such as in uses where such a surface should be chemically inert, have a low tendency to stick to anything in contact with it, be nonstaining, be nontoxic, etc. In particular such items are useful in ovenware, where the nonstick properties of fluoropolymers are well known and appreciated, in chemical process systems where inert surfaces are needed, and where low frictional properties are needed. In many of these uses, such as ovenware, the good high temperature resistance of LCPs makes them particularly useful as the base material for the item, and in such uses it is preferred that the fluoropolymer(s) used in the coating have a melting point above about 250°C so that it too does not melt in use. By ovenware are meant items that may be placed in a thermal and/or microwave oven to cook and/or heat foods at temperatures normally used for such purposes. Items meant to be used in microwave ovens need not have as high a temperature resistance, and here melting points for the LCP and/or fluoropolymer should preferably be >150°C, more preferably >200°C. For other uses, such as in chemical processes, the required melting points of the LCP and fluoropolymer will be determined by temperatures which are reached in the particular use.

Preferably the ovenware or other part is not completely coated (encapsulated) by the fluoropolymer, but coated on one or more surfaces. For example ovenware often comes in the form of bowls or pots, and it is preferable to coat only the inside surface of the bowl or pot. In other words it is preferable to coat only the sur-

face(s) that normally are in contact with the food or food ingredients, especially while being cooked and/or heated. The fluoropolymer coating will preferably therefore be in contact with the food or other material to which the part is exposed. It is particularly important in ovenware uses and other uses that the adhesion of the fluoropolymer to the LCP be retained even after exposure to water, including boiling water, since most food of course contains water.

10 Preferably the LCP part to be coated is melt formed, i.e., injection molded, extruded, melt blown, thermoformed, etc. An injection molded part is a preferred LCP part.

Useful fluoropolymers for the coating include
15 polytetrafluoroethylene, copolymers of tetrafluoroethylene (TFE) such as TFE/perfluoro(propyl vinyl ether), TFE/hexafluoropropylene, TFE/ethylene, and other fluorinated polymers such as poly(vinyl fluoride), and poly(vinylidene fluoride). Preferred fluoropolymers are
20 polyTFE, TFE/perfluoro(propyl vinyl ether), and TFE/hexafluoropropylene, and especially preferred polymers are TFE/perfluoro(propyl vinyl ether), and TFE/hexafluoropropylene.

The LCP may contain other materials which are typically melt mixed with such polymers such as fillers/reinforcing agents such as talc, glass fiber, glass flake, wollastonite, milled glass fiber, glass spheres, calcium sulfate, mica and TiO_2 , colorants and pigments such as carbon black and TiO_2 , stabilizers such as anti-
30 oxidants, and other materials. One or more of these materials may be present in conventional amounts. Before coating with fluoropolymer, the LCP may be formed by any conventional method, particularly melt forming such as

injection molding, compression molding, blow molding, extrusion, and thermoforming.

In some of the Examples, the polymer used had the composition (repeat units) 4,4'-

5 biphenol/hydroquinone/terephthalic acid/2,6-naphthalenedicarboxylic acid/4-hydroxybenzoic acid in a 50/50/87.5/12.5/300 molar ratio. This polymer may be synthesized by methods described in U.S. Patent 5,525,700. In the Examples, the following materials were
10 used:

Jetfil® 575C talc, available from Luzenac America, Inc., Englewood, CO, U.S.A.

Tiona® RCL4 Titanium Dioxide, a chloride process rutile-type TiO₂ surface treated with alumina and an organic substance, available from SMC Corp. of Baltimore,
15 MD, U.S.A.

Ultranox® 626, a phosphorous containing antioxidant, available from GE Specialty Chemicals.

Adhesion of the fluoropolymer coating to the LCP
20 was tested by cutting an "X" through the fluoropolymer coating with a razor blade. A piece of Scotch® Magic Tape #810, 3/4" (1.91 cm) wide, available from 3M Corp., St. Paul, MN, U.S.A., was applied to the area including the "X", using finger pressure and then peeled off. If
25 little or no fluoropolymer coating was removed or peeled loose, adhesion was considered good.

Example 1

Compounding of LCP resins with the talc, TiO₂, Ultranox® 626 phosphite stabilizer was done in a 40 mm ZSK
30 Werner and Pfleiderer twin-screw extruder having a zone with conventional conveying elements, a zone with kneading or mixing elements, and a low pressure zone with

venting under vacuum of any volatiles from the polymer melt, and a die. As the compounded compositions exited the die, they were quenched with a water spray and cut into pellets with a conventional strand cutter. The extruder barrel and die temperatures were maintained at about 340°C. Prior to molding the pellets, the pellets were dried overnight for approximately 16 hours in a vacuum oven with N₂ purge at 100-130°C. The LCP composition contained (all weight percents) 54.7% LCP, 40.0% Jetfil® 575C talc, 5.0% Tiona® RCL4 TiO₂, and 0.30% Ultrinox® 626. The discs were molded on a 6 oz. (171 g) single screw injection molding machine, using a barrel temperature of 345°C, a nozzle temperature of 345-350°C, a mold temperature of 115°C, a screw speed of 120 rpm, a 1.5 sec. injection boost, 5 sec injection, 10 sec. hold time, and mold open of about 3 sec. Injection boost pressure was 35 MPa, injection pressure was 28 MPa, and back pressure was 350 kPa.

Four injection molded discs, 10.2 cm in diameter and 0.16 cm thick, were heat aged in a circulating air oven at 250°C for 8 h, and then at 315°C for 30 min. The discs were coated by EMC Coating, Inc., Newport, DE, U.S.A. using their EMC-128 coating system, which is believed to contain Teflon® FEP, a copolymer of TFE and hexafluoropropylene having a melting point of about 275°C, and available from E. I. DuPont de Nemours & Co., Inc., Wilmington, DE, U.S.A. This fluoropolymer coating was baked onto the LCP at a temperature of 310°C for 30 min. Before application of the fluoropolymer the LCP surface was coated with Teflon® Primer Black, Product Code #420-703, available from E. I. DuPont de Nemours & Co., Inc., Wilmington, DE U.S.A. The fluoropolymer coating adhered well to the LCP. One of the discs was immersed in boil-

ing water for 2 h and after that immersion there was no apparent change in the adhesion of the fluoropolymer to the LCP or to the appearance of the disc.

Example 2

5 The polymer used had the composition (repeat units)
4,4'-biphenol/hydroquinone/terephthalic acid/2,6-
naphthalenedicboxylic acid/4-hydroxybenzoic acid in a
50/50/85/15/300 molar ratio. It was made in the same
manner as the LCP of Example 1. It contained 45% by
10 weight glass fiber and 5 % by weight of TiO₂. Plaques, 10
cm x 10 cm x 3 mm thick were molded by a method similar
to the plaques of Example 1. Two of the plaques were
heated aged for 8 h at 250°C in air. One of these plaques
was coated as in Example 1 with a fluoropolymer , and the
15 other was coated the same way except no primer was used.
A third plaque was heat aged for 8 h at 250°C in nitrogen
and coated with fluoropolymer in a like manner. Good ad-
hesion of the fluoropolymer coating to the LCP was ob-
tained with all 3 plaques.

CLAIMS

What is claimed is:

1. A part made of thermotropic liquid crystalline
5 polymer and coated with a fluoropolymer coating.
2. The part as recited in claim 1 wherein said part
is an ovenware part.
3. The part as recited in claim 1 or 2 wherein said
fluoropolymer is a perfluoropolymer.
- 10 4. The process as recited in claim 3 wherein said
perfluoropolymer is polytetrafluoroethylene or a copoly-
mer of tetrafluoroethylene.

