

Description

Technical Field

This invention concerns low surface energy liners having protective, release, or lubricating function, e.g., low-adhesion backsize coatings that permit pressure-sensitive adhesive tapes to be wound upon themselves for storage and later unwound to be put to use.

Background Art

Pressure-sensitive adhesive tape which is wound upon itself in roll form has a low-adhesion backsize coating to permit the tape to be unwound without delaminating. If the tape is not wound upon itself, its adhesive is customarily protected by a disposable web which likewise has a low-adhesion coating. Any such low-adhesion coating must both adhere strongly to its underlying substrate and be sufficiently cohesive not to contaminate the adhesive, i.e., not to interfere unduly with its adhesiveness. Low-adhesion backsize coatings are disclosed in U.S. Patents No. 3,318,852; 3,536,749; 4,057,596 and 4,216,252.

Certain pressure-sensitive adhesives are so aggressively tacky that tapes require undesirably high peel forces to be removed from known low-adhesion backsize coatings, especially after prolonged storage. Such tapes may carry away and thus be contaminated by appreciable amounts of the low-adhesion material. It is believed that no release coating of the prior art is fully effective for use with aggressively tacky poly(dimethylsiloxane) pressure-sensitive adhesives.

The need for improved low-adhesion coatings is especially acute for pressure-sensitive adhesive tapes having porous backings such as breathable medical tapes. When such tapes are wound upon themselves into roll form, the pressure-sensitive adhesive may gradually flow into the pores of the backing and thus create a mechanical bond that may cause the adhesive layer to split upon unwinding unless the low-adhesion backsize coating is exceedingly effective. For some such tapes it has been necessary to employ a nonporous, disposable, low-adhesion web, the cost of which could have been avoided if a better low-adhesion backsize coating were available.

Pressure-sensitive adhesive transfer tapes which are marketed in roll form usually have a carrier web having low-adhesion coatings on both surfaces, one of which provides a lower unwinding force so that the adhesive layer remains on the carrier web during unwinding. If the pressure-sensitive adhesive is highly aggressive, the low-adhesion coating which is to provide the higher unwinding force must accomplish the aforementioned objectives, and the low-adhesion coating which is to provide the lower unwinding force must be even more effective.

Coatings comparable to low-adhesion backsize coatings have other uses, e.g., nonstick coatings for cooking utensils, ice-releasing coatings for aircraft, and lubricative coatings for magnetic recording media. Such low-adhesion coatings are sometimes called "release coatings", a term which also encompasses release agents for molds, which may be effective only by failing cohesively. Lubricants usually function by cohesive failure. To distinguish release coatings which are designed to fail cohesively from those which are designed to resist cohesive failure, the latter are here called "liners" and, more specifically, "low surface energy liners" because low surface energy is important to their effectiveness.

In EP-A-40923 there is disclosed a substrate primarily for use in an image transfer system in which there is an adhesive coating comprising predominantly a film-forming polymer with a minor amount of a fluoroacrylate similar to that of the present invention. There is no discussion of a liner consisting only of polymer containing at least 75 weight per cent of perfluoropolyether segments.

Disclosure of Invention

The present invention provides a low surface energy liner which is effective as a low-adhesion coating for use with the most aggressive pressure-sensitive adhesives without unduly diminishing their adhesiveness.

Briefly, the present invention concerns a substrate having a liner comprising an insoluble polymer of polymerized, film-forming monomer having a polymerizable functionality greater than 1 and a perfluoropolyether segment which is a plurality of perfluoroalkylene oxide, $-C_nF_{2n}O-$, repeating units, where n in each such unit is independently an integer from 1 to 4, which segment preferably has a number average molecular weight of 500 to 20,000 said segments being at least 75% by weight of said liner.

The monomer can be *in-situ* polymerized, i.e., polymerized in place on the substrate. The *in-situ* polymerized liner resists transfer when used as a low-adhesion coating for an aggressively pressure-sensitive adhesive tape. Even though the thickness of the polymer liner may be ultra-thin or so thin as to be virtually monomolecular, it provides a barrier or liner which effectively prevents the most aggressive pressure-sensitive adhesives from becoming appreciably bonded to the underlying substrates, even after prolonged storage. While being exceedingly difficult to measure, preferred thicknesses of the low surface energy liner of the invention are in the approximate range of 5 to 500 nm (nanometers), more preferably within 10 to 100 nm. Although perfluoropolyether monomers are exceedingly expensive, so little material is used in making such thin coatings that the low surface energy liners would be costwise competitive with comparable liners of the prior art.

The low surface energy liner of the invention may be applied to a substrate by the steps of
(a) providing a dilute solution of a polymerizable monomer having an average polymerization

functionality greater than 1 and comprising a perfluoropolyether segment which comprises $-\text{C}_a\text{F}_{2a}\text{O}-$ repeating units, where a in each such unit is independently an integer from 1 to 4, and preferably has a number average molecular weight of 500 to 20,000 said segments being at least 75% by weight of said monomer,

- 5 (b) coating said solution onto the substrate,
(c) drying the coating (to remove solvent), and
(d) *in-situ* polymerizing the monomer.

The resulting polymer liner comprises a cohesive network of perfluoropolyether segments, adhered to the substrate, said polymer preferably being an addition polymer.

- 10 When the perfluoropolyether monomer has polymerizable functional groups having ethylenic unsaturation such as acryloyl, polymerization can be effected by exposing the coated substrate to ultraviolet radiation, preferably in an inert atmosphere. Usually the whole process can be carried out in-line, but some difficulty has been encountered in obtaining a sufficiently inert atmosphere for dried coatings greater than 200 nm in thickness.

- 15 When the perfluoropolyether monomer has hydrolyzable silane, epoxy, or isocyanate polymerizable groups, thermal polymerization can be employed by exposing the coated substrate to thermal radiation. When the polymerizable groups are epoxy, ultraviolet radiation may be employed in air in the presence of an aromatic onium salt polymerization catalyst, such as diphenyliodonium hexafluoroantimonate or triphenylsulfonium hexafluoroantimonate, incorporated into the coating solution.

- 20 In any event, the polymer, making up the liner is insoluble (that is, crosslinked), as manifested by its insolubility in "Freon" 113 (1,1,2-trichloro-2,2,1-trifluoroethane) at 20°C.

- The thickness of the low energy liner is conveniently controlled by the proportion of solvent in the solution from which the perfluoropolyether monomer is coated. Coating techniques useful for in-line processing include brushing, wire or knife coating, spraying, curtain coating and gravure coating. While the thickness of the low energy liner is preferably less than 500 nm because of the high cost of perfluoropolyether monomer, much greater thicknesses are equally useful, and it may be as thin as 5 or 10 nm. The particular thickness used will also depend on the particular application or utility of the liner.

- The perfluoropolyether segments in the polymer form a cohesive network which apparently becomes bonded to the contiguous substrate at a large number of points, and even though the bonds may be individually quite weak, together they adequately adhere the network to the substrate.

- Suitable substrates to which the coating can be applied include, for example, paper, glass, steel, aluminum, plastics such as polyester, polyvinyl chloride, non-woven fabrics and the like. For those applications in which the release coated article is to be a pressure-sensitive tape or sheet, it is desirable that the substrate be flexible.

- 35 The low surface energy liners of the invention are useful in a variety of other applications such as nonstick coatings for cooking utensils, ice-releasing coatings for aircraft, and lubricative coatings for magnetic recording media.

If the low surface energy liner does not adhere well to the substrate, it may be desirable to apply first a primer or an adhesion-promoting coating, as is well-known in the art.

- 40 Suitable perfluoropolyether monomers for making the low surface energy liner of the invention have the formula

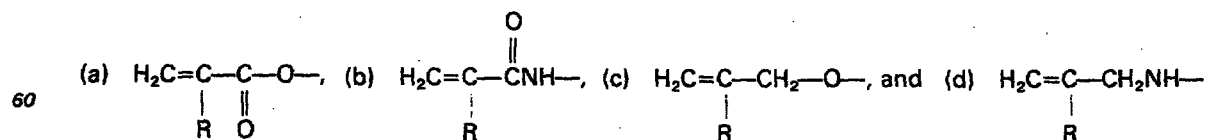


- 45 wherein Q comprises a polymerizable (preferably addition polymerizable) group attached to a chain or randomly distributed perfluoroalkylene oxide, $-\text{C}_a\text{F}_{2a}\text{O}-$, repeating units, in each of which a is independently an integer of 1 to 4, k is the number of such repeating units and it has a value from 1 to 300 such that the segment preferably has a number average molecular weight of 500 to 20,000, and Z is $-\text{OC}_a\text{F}_{2a+1}$ or Q. If Z is not Q, it preferably is $-\text{OCF}_3$, $-\text{OCF}_2\text{CF}_3$, or $-\text{OCF}(\text{CF}_3)\text{CF}_3$. Typically the perfluoroalkylene oxide units will be $-\text{CF}_2\text{O}-$, $-\text{C}_2\text{F}_4\text{O}-$, and/or $-\text{C}_3\text{F}_6\text{O}-$.

It is preferred that the perfluoropolyether monomers have functionalities within the range of 1.5 to 2.0 in order to provide covalent bonding at both ends of most of the segments.

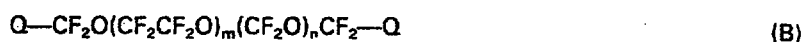
Preferred perfluoropolyether monomers are the ethylenically-unsaturated monomers disclosed in U.S. Patent No. 3,810,874 (Mitsch et al.) and U.S. Patent No. 4,321,404 (Williams et al.) wherein Q of the above

- 55 Formula A is selected from



- 65 where R is hydrogen or methyl.

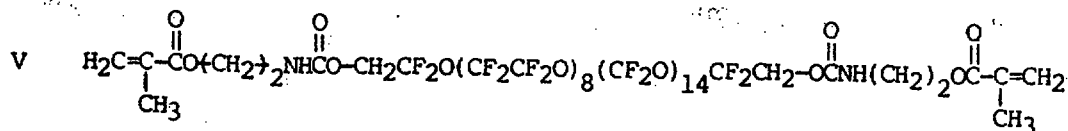
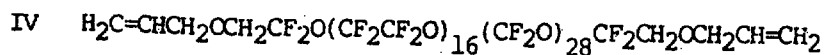
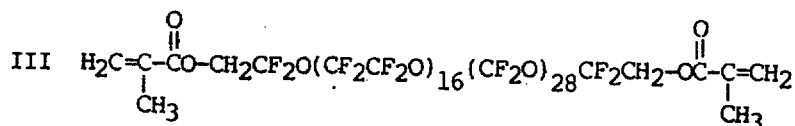
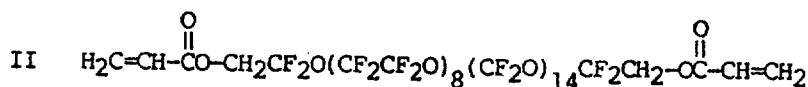
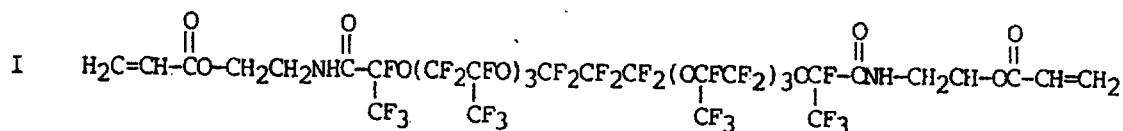
These preferred ethylenically-unsaturated perfluoropolyether monomers which have the formula

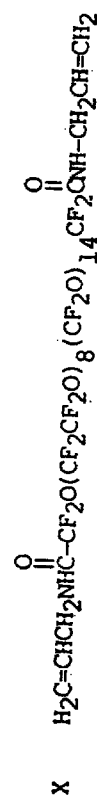
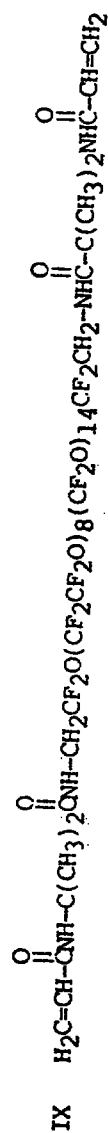
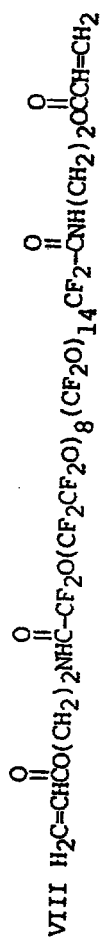
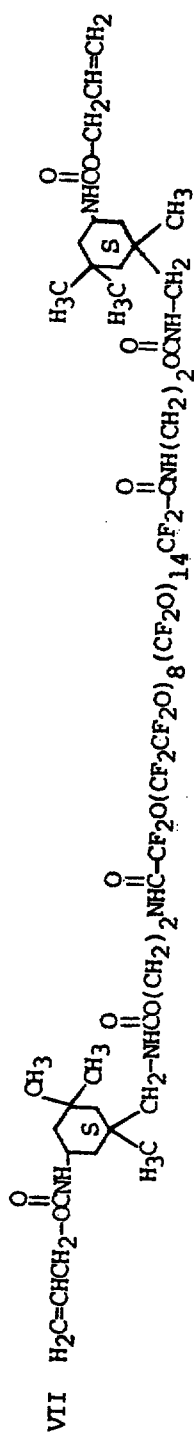
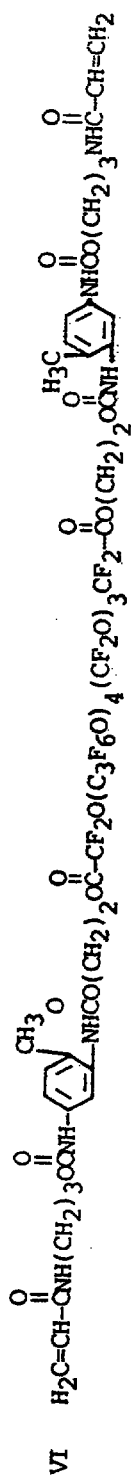


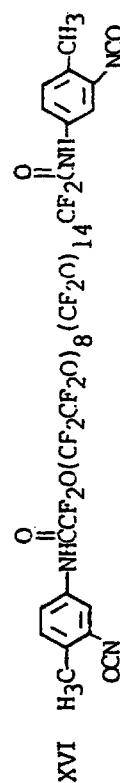
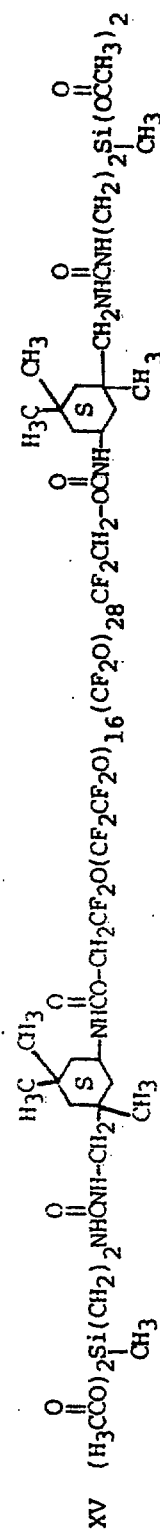
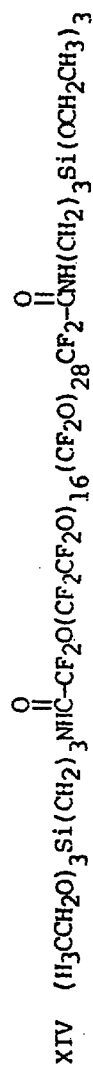
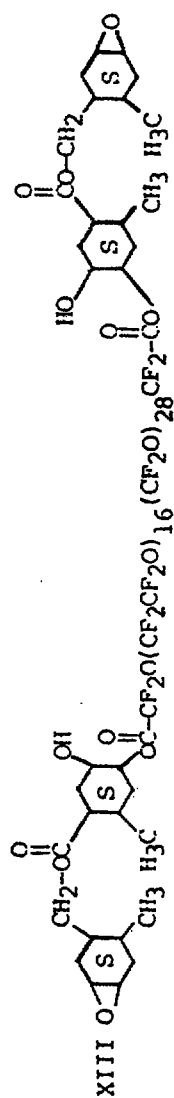
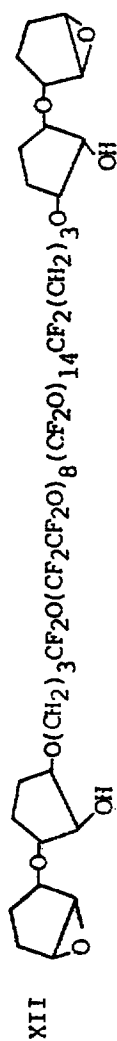
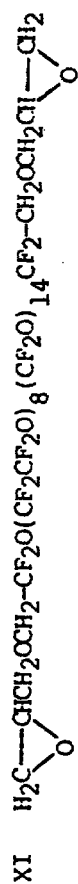
wherein Q is as defined above and m and n designate the number of randomly distributed perfluoroethyleneoxy and perfluoromethylene oxy backbone repeating units, respectively, n and m having independently values, for examples, from 1 to 200 and the ratio m/n is 0.2/1 to 5/1.

Examples of polymerizable perfluoropolyether monomers of Formula A useful for making the low-energy liner of the invention are those of the following where here again, as elsewhere, the perfluoroalkylene oxide units are randomly distributed, the given numbers of which are average values.

Perfluoropolyether Monomer







Further description of such monomers, and their preparation, will be omitted in the interest of brevity, the disclosure of said U.S. Patent Nos. 3,810,874 and 4,321,404 being incorporated herein for such purposes.

In making a low surface energy liner of the invention, one or more other types of monomers copolymerizable with the perfluoropolyether monomer may be dissolved into the solution in amounts providing up to about 20% by weight of the low-energy liner. However, the liner is most effective if the amount of the perfluoropolyether monomer is such that at least 75% of the liner's weight is provided by perfluoropolyether segments. When the perfluoropolyether monomer has polymerizable groups which are ethylenically unsaturated, useful copolymerizable monomers include acrylic and methacrylic esters, amides, and urethanes, and vinyl ethers, epoxides, and heterocycles.

When Q of Formulae A or B is a 1,2-epoxy group, useful copolymerizable monomers include 1,2-epoxy-substituted esters, ethers, siloxanes, and nitriles such as listed in columns 3 and 4 of U.S. Patent No. 4,219,377.

When Q of Formulae A or B is a hydrolyzable silane group, useful copolymerizable monomers include silanes which may be linear or cyclic and may have alkoxy, halo, cyano, aceto, methacryloxy, lower alkenyl, or phenyl substituents.

When Q of Formulae A or B is an isocyanato group, useful copolymerizable monomers include isocyanates, polyols, and polyamines.

Examples

The invention will be illustrated by the following examples. In these examples the tests for "Release Peel Force", "Readhesion Peel Force" and "Control Peel Force" were made using a roll of pressure-sensitive adhesive tape having an aggressive poly(dimethylsiloxane) pressure-sensitive adhesive (Dow Corning DC 284), 0.025 mm in thickness. Its backing was biaxially-oriented poly(ethyleneterephthalate) film 0.038 mm in thickness and having no low-adhesion backsize coating.

In determining Release Peel Force, the pressure-sensitive adhesive layer of a piece of the test tape was pressed against the low surface energy liner using a smooth plastic bar. After simulated aging at an elevated temperature and cooling to 22°C, the underlying film was pressed against a layer of pressure-sensitive adhesive carried by a rigid plate, thus rigidifying the low surface energy liner. The test tape was then peeled back at an angle of 180° and at 2.3 m/min., and the peel back force (the "Release Peel Force") was measured after the peeling had begun.

After being peeled off, the pressure-sensitive adhesive tape was adhered to a clean glass plate using two passes of a 2-kg hand rubber roller, and the 180° peel back force (the "Readhesion Peel Force") was again measured at 2.3 m/min.

Another piece of the test tape was adhered to a clean glass plate and tested in the same way as in the previous test to provide the "Control Peel Force". Any appreciable reduction in Readhesion Peel Force versus Control Peel Force was presumed to result from appreciable transfer of low-energy liner material to the pressure-sensitive adhesive.

The following examples employ the perfluoropolyether monomers listed above, some of which were first modified as indicated below:

Perfluoropolyether

- | | |
|-------|--|
| XVII | Perfluoropolyether II (80 parts) plus 20 parts of methacrylic acid |
| XVIII | Perfluoropolyether III (80 parts) plus 20 parts of 2-hydroxyethyl methacrylate |

In the examples, all parts are by weight.

Example 1

A 1% solution of Perfluoropolyether Monomer II in 1,1,2-trichloro-1,2,2-trifluoroethane ("Freon" 113) was coated onto biaxially-oriented poly(ethyleneterephthalate) film using a wire-wound rod and allowed to dry under ambient conditions to provide a low-energy liner. Its calculated thickness was about 70 nm. While under a nitrogen atmosphere and at a speed as indicated in Table A below, the coated film was irradiated with ultraviolet light from a pair of medium-pressure mercury lamps at 80 watts per cm using an ultraviolet processor from PPG Industries, Model QC 1202AN3IR. This polymerized the perfluoropolyether *in situ* to provide a low-energy liner which was tested after simulated aging at 70°C for 24 hours using a poly(dimethylsiloxane) pressure-sensitive adhesive tape made from Dow Corning DC 284 having an adhesive thickness of 0.025 mm. Results were

Release Peel Force	<0.2N/dm
Readhesion Peel Force	40—45N/dm
Control Peel Force	40—43N/dm

Examples 2—7

A number of low surface energy liners of the invention were made in the same way as in Example 1 except as indicated in Table A which also reports test values.

TABLE A

Example	Perfluoro-polyether	Low-energy liner thickness (nm)	Speed (m/min)	Peel Forces (N/dm)		
				Release	Readh.***	Control
1	II	70	25	<0.2	40—45	40—43
2	II	14	18	1.0—1.4	49	40—43
3	V	34	25**	2.0—3.0	40—50	39—42
4	XVII	70	25	2.0—3.0	36—38	39—42
5	XVIII	70	25	2.0—3.0	35—37	39—42
6	IV*	70	25	2.0—4.0	29—45	39—42
7	X*	70	25	2.0—6.0	34—45	39—42

* Solution also contained 5 parts of 2,4-bis(trichloromethyl)-6-(4-methoxyphenyl)-s-triazine per 95 parts of the perfluoropolyether monomer.

** Two passes.

*** "Readh." means readhesion.

Example 8

A 1% solution in "Freon" 113 containing 99 parts of Perfluoropolyether Monomer II and 1 part of benzildimethylketal was coated onto 0.1 mm biaxially-oriented poly(ethyleneterephthalate) film using a wire-wound rod and allowed to dry under ambient conditions to give a calculated dry thickness of about 70 nm. The coated film was placed inside a container equipped with nitrogen inlet and outlet at a distance of 7.6 cm below a 5 mm Prex glass plate cover. A 275 watt sun lamp from General Electric (order code RS) was positioned 18 cm above the glass plate. The container was flushed with nitrogen for 15 min. and the lamp allowed to warm up before removing a shutter to expose the coating. The coating was irradiated for the length of time indicated in Table B. This polymerized the perfluoropolyether *in situ* to provide a low surface energy liner which was tested after simulated aging using the Test Tape. Results were:

Release Peel Force	0.8—2 N/dm
Readhesion Peel Force	48 N/dm
Control Peel Force	40—43 N/dm

Examples 9—11

A number of low surface energy liners of the invention were made in the same way as in Example 8 except that the poly(ethyleneterephthalate) film had on it a primer coating of poly(vinylidenedichloride). Test results are reported in Table B.

TABLE B

Ex.	Perfluoro-polyether	Low Surface energy liner Thickness (nm)	Irradiation Time (min)	Peel Forces (N/dm)		
				Release	Read.	Control
8	II	68	2	0.8—2.0	48	40—43
9	II	1700	2	1.1	54	55
10	III	1700	25	0.6	49—54	49—54
11	VIII	1700	5	4.4	54	49—54

Example 12

A 25% solutes solution in "Freon" 113 containing 99 parts Perfluoropolyether Monomer II and 1 part benzildimethylketal was coated onto 0.1 mm biaxially-oriented poly(ethyleneterephthalate) film using a wire-wound rod and allowed to dry under ambient conditions to give a calculated thickness of 1.7 micrometers. The coating was irradiated for 10 min. under nitrogen using a sunlamp as described in Example 8 to provide a low surface energy liner. A solution containing 100 parts DC 284 poly(dimethylsiloxane), 75 parts toluene, 25 parts heptane and 1.2 parts of a 50/50 mixture of 2,4-dichlorobenzoyl peroxide/dibutyl phthalate was coated onto the low-energy liner using a knife coater. After allowing most of the solvent to evaporate under ambient conditions, the composite was placed in a 138°C oven for 5 min. to provide a silicone pressure-sensitive adhesive cured *in situ* on the low surface energy liner. The dry thickness of the adhesive was 0.1 mm. A 0.038 mm film of poly(ethyleneterephthalate) was then laminated to the adhesive, thus creating a pressure-sensitive adhesive tape adhered to the low surface energy liner. After simulated aging at 70°C for 20 hours and cooling to 22°C, the tape was peeled back with the following results:

15	Release Peel Force	16—19 N/dm
	Readhesion Peel Force	12—24 N/dm
	Control Peel Force	56 N/dm

Example 13

The procedure of Example 12 was repeated except that the 25% solutes coating solution contained 94 parts of the Perfluoropolyether Monomer II, 5 parts of an inert perfluoropolyether (Braycote 815Z), and 1 part of benzildimethylketal. After simulated aging at 70°C for 20 hours and cooling to 22°C, the tape was peeled back with the following results:

25	Release Peel Force	3.4—5.6 N/dm
	Readhesion Peel Force	29—46 N/dm
	Control Peel Force	56 N/dm

Example 14

A 0.5% solutes solution in 80/20 "Freon" 113/acetone containing 99 parts of Perfluoropolyether Monomer XI and 1 part of triphenylsulfonium hexafluoroantimonate was coated onto 0.1 mm biaxially-oriented poly(ethyleneterephthalate) film using a wire-wound rod and allowed to dry under ambient conditions to give a calculated thickness of 34 nm. The coating was irradiated in an air atmosphere using the ultraviolet processor described in Example 1 using two lamps at 80 watts/cm each and a speed of 25 m/min. The low surface energy coating was tested using the Test Tape after being in contact with the low surface energy liner for 4 hours under ambient conditions. Results were:

40	Release Peel Force	0.8—1.6 N/dm
	Readhesion Peel Force	36—42 N/dm
	Control Peel Force	39—42 N/dm

Example 15

6.8 g of a 8.3% solutes solution in "Freon" 113 containing 99 parts of the solutes of Perfluoropolyether Monomer XVI and 1 part 1-methylimidazole was poured into a 14.5 cm diameter petri dish. The solvent was allowed to evaporate under ambient conditions, and the residue allowed to stand under ambient conditions (50—65% relative humidity, 22°C) for three days, thus providing a low surface energy liner having a thickness of about 12 micrometers. The low surface energy coating was tested using the Test Tape after being in contact for 24 hours at 68°C. Results were:

50	Release Peel Force	1.3—2.6 N/dm
	Readhesion Peel Force	30—36 N/dm
	Control Peel Force	39—42 N/dm

Example 16

To one gram of Perfluoropolyether XIV was added 0.2 g of tetraethylorthosilicate and 0.2 g of a 10% solution of dibutyltin diacetate in methyl ethyl ketone. This solution was coated onto biaxially-oriented poly(ethyleneterephthalate) film of 0.038 mm thickness using a wire-wound rod. The coated film was placed in a 90°C oven for 3 min. to dry the coating and to polymerize it *in situ* to provide a low surface energy liner about 2500 nm in thickness.

This low-energy liner was tested as described in Example 12, with the following results:

65	Release Peel Force	0.2 N/dm
	Readhesion Peel Force	55 N/dm
	Control Peel Force	65 N/dm

Claims

1. A substrate having a liner, characterized in that said liner is a low surface energy liner in the form of a coating on said substrate consisting of an insoluble polymer comprising perfluoropolyether segments which are a plurality of $-\text{C}_a\text{F}_{2a}\text{O}-$ repeating units, wherein each such unit a is an integer from 1 to 4, and segments being at least 75 percent of the weight of said liner.

2. A substrate as defined in claim 1 further characterized by the feature that said perfluoropolyether segment is



wherein m and n denote randomly distributed repeating units and the ratio m/n is 0.2/1 to 5/1.

3. A substrate as defined in claim 1 further characterized by the feature that said segment has a number average molecular weight of 500 to 20,000.

4. A substrate as defined in claim 1 further characterized by the feature that said liner is an adherent, cohesive liner of low surface energy, 5 to 500 nanometers in thickness, prepared from monomer polymerized *in situ* on said substrate in the form of a coating, and comprising an insoluble addition polymer which comprises a plurality of perfluoropolyether segments of the formula



where m and n denote randomly distributed repeating units and the ratio m/n is 0.2/1 to 5/1, said segment having a number average molecular weight of 800 to 10,000.

5. A substrate according to any one of claims 1 to 4 wherein the substrate is a flexible plastic film.

6. A substrate according to any one of claims 1 to 5 wherein the substrate is a polyethyleneterephthalate film.

7. An article according to any one of claims 1 to 6 in the form of a pressure-sensitive adhesive tape comprising a flexible web having a pressure-sensitive adhesive layer and said liner is a low adhesion backsize liner.

8. An article according to claim 7 wherein the adhesive layer is an aggressive poly (dimethylsiloxane) pressure sensitive adhesive layer and said liner is a low adhesion backsize liner.

9. An article according to any one of claims 1 to 6 wherein the substrate is a magnetic recording medium.

10. Method of making the substrate of claim 1 characterized by the steps comprising

(a) providing a dilute solution of a polymerizable monomer having a polymerizable functionality greater than 1 and comprising perfluoropolyether segments which are a plurality of $-\text{C}_a\text{F}_{2a}\text{O}-$ repeating units, where a is independently in each such unit an integer from 1 to 4, segments by at least 75% of the weight of said monomer,

(b) coating said solution onto the substrate,

(c) drying the coating, and

(d) *in-situ*-polymerizing the monomer to provide an insoluble, cohesive polymer which polymer is adhered to the substrate.

11. Method as defined in claim 10 further characterized by the feature that said monomer has the formula

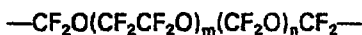


wherein Q comprises a polymerizable group attached to a chain of k randomly distributed $-\text{C}_a\text{F}_{2a}\text{O}-$ repeating units, where a is independently in each such unit an integer of 1 to 4, and Z is $-\text{OC}_a\text{F}_{2a+1}$ or Q .

12. Method as defined in claim 10 further characterized by the feature that said monomer has a functionality within the range of 1.5 to 2.0

13. Method as defined in claim 12 further characterized by the feature that said functionality of said monomer is ethylenic unsaturation, and the polymerizing step (d) involves exposing the dried coating to ultraviolet radiation.

14. Method as defined in claim 12 further characterized by the feature that said perfluoropolyether segment is



wherein m and n denote randomly distributed repeating units, the ratio m/n is 0.2/1 to 5/1, and wherein said monomer has a plurality of acryloyl groups.



Patentansprüche

1. Substrat mit einer Abdeckung, dadurch gekennzeichnet, daß die Abdeckung eine Abdeckung mit niedriger Oberflächenenergie ist und aus einem auf dem Substrat vorgesehenen Überzug aus einem unlöslichen Polymer mit Perfluorpolyethersegmenten besteht, die aus einer Mehrzahl von wiederkehrenden Einheiten $-\text{C}_a\text{F}_{2a}\text{O}-$ bestehen, dadurch gekennzeichnet, daß in jeder dieser Einheiten a eine ganze Zahl von 1 bis 4 ist und die Abdeckung zu mindestens 75 Gew.% aus den genannten Segmenten besteht.

2. Substrat nach Anspruch 1, dadurch gekennzeichnet, daß das Perfluorpolyethersegment



ist, wobei m und n unregelmäßig verteilte, wiederkehrende Einheiten berechnen und das Verhältnis m/n 0,2/1 bis 5/1 beträgt.

3. Substrat nach Anspruch 1, dadurch gekennzeichnet, daß das Segment ein zahlenmäßig durchschnittliches Molekulargewicht von 500 bis 20 000 hat.

4. Substrat nach Anspruch 1, dadurch gekennzeichnet, daß die genannte Abdeckung eine anhaftende, kohärente Abdeckung mit niedriger Oberflächenenergie ist, eine Dicke von 5 bis 500 nm hat und aus einem auf dem Substrat in Form eines Überzuges in situ polymerisierten Monomer besteht und mindestens teilweise aus einem unlöslichen Additionspolymerisat besteht, das eine Mehrzahl von Perfluorpolyethersegmenten der Formel



besitzt, in der m und n unregelmäßig verteilte, wiederkehrende Einheiten bezeichnen und als Verhältnis m/n 0,2/1 bis 5/1 beträgt, und wobei das genannte Segment ein zahlenmäßig durchschnittliches Molekulargewicht von 800 bis 10 000 hat.

5. Substrat nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Substrat ein flexibler Kunststoffilm ist.

6. Substrat nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Substrat ein Polyethylenterephthalatfilm ist.

7. Artikel nach einem der Ansprüche 1 bis 6 in Form eines Haftklebebandes mit einer flexiblen Materialbahn, die mit einer Haftkleberschicht versehen ist, wobei die Abdeckung eine rückseitig nur schwach klebende Abdeckung ist.

8. Artikel nach Anspruch 7, dadurch gekennzeichnet, daß die Kleberschicht aus einem aggressiven Haftkleber auf der Basis von Poly(dimethylsiloxan) besteht.

9. Artikel nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Substrat ein magnetischer Aufzeichnungsträger ist.

10. Verfahren zum Herstellen des Substrats nach Anspruch 1, gekennzeichnet, durch folgende Schritte:

(a) es wird eine verdünnte Lösung eines polymerisierbaren Monomers verwendet, deren polymerisierbare Funktionalität größer ist als 1 und die Perfluorpolyethersegmente besitzt, die aus einer Mehrzahl von wiederkehrenden Einheiten $-\text{C}_a\text{F}_{2a}\text{O}-$ bestehen, wobei a in jeder dieser Einheiten unabhängig von den anderen eine ganze Zahl von 1 bis 4 ist und das Monomer zu mindestens 75 Gew.% aus den genannten Segmenten besteht,

(b) die genannte Lösung wird auf das Substrat aufgetragen,

(c) der so erhaltene Überzug wird getrocknet und

(d) durch Polymerisieren des Monomers in situ wird ein unlösliches kohärentes, vernetztes Polymer gebildet, das an dem Substrat haftet.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Monomer die Formel

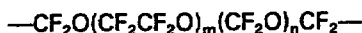


hat, in der Q eine polymerisierbare Gruppe ist, die an einer Kette von k unregelmäßig verteilten, wiederkehrenden Einheiten $-\text{C}_a\text{F}_{2a}\text{O}-$ angelagert ist, a in jeder dieser Einheiten unabhängig von den anderen eine ganze Zahl von 1 bis 4 ist und Z $-\text{OC}_a\text{F}_{2a+1}$ oder Q ist.

12. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Monomer eine Funktionalität im Bereich von 1,5 bis 2,0 hat.

13. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß die Funktionalität des Monomers eine ethylenische Ungesättigkeit ist und in dem Polymerisierungsschritt (d) der getrocknete Überzug einer Ultraviolettstrahlung ausgesetzt wird.

14. Verfahren nach Anspruch 12, dadurch gekennzeichnet, daß das Perfluorpolyethersegment



ist, m und n unregelmäßig verteilte, wiederkehrende Einheiten bezeichnen, das Verhältnis m/n 0,2/1 bis 5/1 beträgt und das Monomer eine Mehrzahl von Acryloylgruppen besitzt.



Revendications

1. Support comportant une doublure, caractérisé en ce que cette doublure est une doublure à faible énergie superficielle sous forme d'un revêtement sur ce support et consistant en un polymère insoluble comprenant des segments de perfluoropolyéther qui sont constitués par une série de chaînons de $-C_aF_{2a}O-$, où a représente, dans chacun de ces maillons, un nombre entier de 1 à 4, les segments constituant au moins 75% du poids de la doublure.

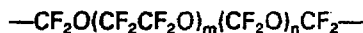
2. Support suivant la revendication 1, caractérisé en outre en ce que le segment de perfluoropolyéther répond à la formule:



dans laquelle m et n désignent des chaînons répartis de façon désordonnée, le rapport m/n étant de 0,2/1 à 5/1.

3. Support suivant la revendication 1, caractérisé en outre en ce que le segment susdit a un poids moléculaire numérique moyen de 500 à 20.000.

4. Support suivant la revendication 1, caractérisé en outre en ce que la doublure est une doublure adhérente, cohérente, de faible énergie superficielle, d'une épaisseur de 5 à 500 nanomètres, cette doublure étant préparée au départ d'un monomère polymérisé in situ sur le support sous la forme d'un revêtement, et comprenant un polymère d'addition insoluble qui comporte une série de segments de perfluoropolyéther de la formule:



dans laquelle m et n désignent des chaînons répartis de façon désordonnée et le rapport m/n est de 0,2/1 à 5/1, ces segments ayant un poids moléculaire numérique moyen de 800 à 10.000.

5. Support suivant l'une quelconque des revendications 1 à 4, caractérisé en ce qu'il est constitué par un film flexible en matière plastique.

6. Support suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que le support est constitué par un film de téréphtalate de polyéthylène.

7. Article suivant l'une quelconque des revendications 1 à 6, sous forme d'un ruban adhésif auto-collant ou adhérent par pression, caractérisé en ce qu'il comprend une feuille continue flexible comportant une couche d'adhésif adhérent par pression la doublure précitée étant une doublure d'apprêt arrière de faible adhérence.

8. Article suivant la revendication 7, caractérisé en ce que la couche d'adhésif est constituée par un adhésif agressif de poly(diméthylsiloxane) adhérent par pression.

9. Article suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que le support est constitué par un matériel d'enregistrement magnétique.

10. Procédé de fabrication du support suivant la revendication 1, caractérisé en ce qu'il comprend les phases suivantes:

(a) la prévision d'une solution diluée d'un monomère polymérisable présentant une fonctionnalité de polymérisation supérieure à 1 et comprenant des segments de perfluoropolyéther qui sont constitués par une série de chaînons de $-C_aF_{2a}O-$, où a représente indépendamment, dans chaque chaînon, un nombre entier de 1 à 4, les segments constituant au moins 75% du poids du monomère susdit,

(b) l'application de cette solution sur le support,

(c) le séchage du revêtement, et

(d) la polymérisation in situ du monomère pour former un polymère cohérent insoluble dont le réseau adhère au support.

11. Procédé suivant la revendication 10, caractérisé en outre en ce que le monomère susdit répond à la formule:



dans laquelle Q comprend un groupe polymérisable attaché à une chaîne de k chaînons de $-C_aF_{2a}O-$ répartis de façon désordonnée, où a désigne indépendamment, dans chaque chaînon, un nombre entier de 1 à 4, et Z représente $-OC_aF_{2a+1}$ ou Q .

12. Procédé suivant la revendication 10, caractérisé en ce que le monomère susdit a une fonctionnalité de l'ordre de 1,5 à 2,0.

13. Procédé suivant la revendication 12, caractérisé en outre en ce que la fonctionnalité susdite du monomère est une insaturation éthylénique, et la phase de polymérisation (d) comprend l'exposition du revêtement séché à un rayonnement ultraviolet.

14. Procédé suivant la revendication 12, caractérisé en outre en ce que le segment de perfluoropolyéther est de la formule:



où m et n désignent des chaînons répartis de façon désordonnée, le rapport m/n étant de 0,2/1 à 5/1, le monomère susdit comportant une série de groupes acryloyle.

