

# PATENT SPECIFICATION

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## (54) SHAPED ARTICLES OF CROSS-LINKED FLUOROCARBON POLYMERS

(71) We, RAYCHEM CORPORATION, A Corporation organised according to the laws of the State of California, United States of America, of 300 Constitution Drive, Menlo Park, California 94025, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to shaped articles of cross-linked fluorocarbon polymers.

It is known to prepare shaped articles of cross-linked polymers by shaping the non-cross-linked polymer and exposing the shaped article to ionising radiation. When this process is applied to fluorocarbon polymers, however, the polymer is not only cross-linked but also degraded by the radiation, and the final product has poor physical properties. It is known that this disadvantage can be mitigated by mixing a cross-linking agent (also known as a coagent) with the fluorocarbon polymer before it is shaped, but the physical properties of the known products are still not entirely satisfactory, especially when the shaping process involves temperatures above 200°C or more, particularly above 250°C., as is often desirable or necessary when melt-shaping fluorocarbon polymers. In particular, the known methods do not provide products which combine high tensile strength at room temperature with the high level of cross-linking needed for good physical properties at temperatures above the melting point of the polymer.

The present invention overcomes the shortcomings of the prior art and in its broadest aspect provides a shaped article of a cross-linked polymeric composition wherein the polymer is a fluorocarbon polymer having a melting point prior to cross-linking of at least 200°C., the article having an  $M_{100}$  value of at least 300 psi (21 kg/cm<sup>2</sup>) and a tensile strength at room temperature of at least 3,000 psi (210 kg/cm<sup>2</sup>), preferably at least 5,000 psi (350 kg/cm<sup>2</sup>). The  $M_{100}$  value, which is a static modulus value above the melting point of the polymer and which is determined by the method described below, provides a measure of the extent of cross-linking. We have found that such shaped articles show outstanding physical properties, and that these properties are especially useful when the shaped article is in the form of an insulating coating on a wire.

The invention also includes a first process for preparing such a shaped article which comprises

(1) contacting (a) a shaped article of a polymeric composition wherein the polymer is a fluorocarbon polymer having a melting point of at least 200°C, the article having a tensile strength of at least 3,000 psi (210 kg/cm<sup>2</sup>), with (b) a fluid composition comprising a cross-linking agent, until the article contains at least 2.5% by weight of the cross-linking agent; and

(2) irradiating the shaped article with ionising radiation to a dosage not exceeding 50 Mrads under conditions such that the composition is cross-linked

sufficiently to impart thereto an  $M_{100}$  value of at least 300 psi (21 kg/cm<sup>2</sup>), while maintaining a tensile strength of at least 3,000 psi (210 kg/cm<sup>2</sup>) the shaped article containing at the commencement of the irradiation at least 2.5% by weight of the cross-linking agent.

5 The invention further includes a second process for preparing a shaped article according to the invention, which process comprises 5

(A) contacting (a) a shaped article of a polymeric composition wherein the polymer is a fluorocarbon polymer having a melting point of at least 200°C, the article having a tensile strength at 25°C of at least 3,000 psi (210 kg/cm<sup>2</sup>), with (b) a fluid composition comprising a cross-linking agent, until the article has adsorbed 10 at least 0.5% by weight of the cross-linking agent; and 10

(B) irradiating the shaped article to a dosage not exceeding 50 Mrads to cause cross-linking thereof while maintaining a tensile strength at 25°C of at least 3,000 psi (210 kg/cm<sup>2</sup>), the shaped article containing at the commencement of the irradiation at least 0.5%, preferably at least 2%, especially at least 4%, by weight of cross-linking agent adsorbed in step (A); and repeating steps (A) and (B) in 15 sequence until the cross-linked shaped article has an  $M_{100}$  value of at least 300 psi (21 kg/cm<sup>2</sup>). 15

It will be noted that steps (A) and (B) of this process are similar to (and can be identical with) steps (1) and (2) of the first process defined above, but that because 20 steps (A) and (B) are repeated at least once, the minimum amount of cross-linking agent present at the beginning of step (B) is less than the minimum amount at the beginning of step (2), and it is only after the final irradiation step that an  $M_{100}$  value of at least 300 psi (21 kg/cm<sup>2</sup>) is required. We have found that by use of this 25 sequential process, shaped articles having remarkably high  $M_{100}$  values can be obtained, for example greater than 1,000 psi (70 kg/cm<sup>2</sup>) and even higher, e.g. greater than 2,500 psi (175 kg/cm<sup>2</sup>). The fluid composition comprising a cross-linking agent used in the repetitions of step (A) will usually be the same as in step (A) but can be different. Likewise the conditions in the repetitions of step (B) can 30 be the same as or different from those in step (B). 30

The term "fluorocarbon polymer" is used herein to denote a polymer or mixture of polymers which contains more than 10%, preferably more than 25%, by weight of fluorine and which contains at least 50% by weight of at least one crystalline fluorine-containing polymers. Thus the fluorocarbon polymer may be a 35 single fluorine-containing polymer, a mixture of two or more fluorine-containing polymers or a mixture of one or more fluorine-containing polymers with one or more polymers which do not contain fluorine. Preferably the fluorocarbon polymer comprises at least 50%, particularly at least 75%, especially at least 85%, by weight of one or more thermoplastic crystalline polymers each containing at 40 least 25% by weight of fluorine, a single such crystalline polymer being preferred. 40 Such a fluorocarbon polymer may contain, for example, a fluorine-containing elastomer and/or a polyolefin, preferably a crystalline polyolefin, in addition to the crystalline fluorine-containing polymer or polymers. The fluorine-containing 45 polymers are generally homo- or co-polymers of one or more fluorine-containing olefinically unsaturated monomers, or copolymers of one or more such monomers with one or more olefins. The fluorocarbon polymer has a melting point of at least 200°C, and will often have a melting point of at least 250°C, e.g. up to 300°C., the melting point being defined for crystalline polymers as the temperature above 50 which no crystallinity exists in the polymer (or when a mixture of crystalline polymers is used, in the major crystalline component in the mixture). Preferably 50 the polymeric composition has a viscosity of less than 10<sup>5</sup> poise at a temperature not more than 60°C above its melting point. A preferred fluorocarbon polymer is a crystalline copolymer of ethylene and tetrafluoroethylene and optionally one or 55 more other comonomers (known as ETFE polymers), especially a copolymer comprising 35 to 60 mole percent of ethylene, 35 to 60 mole percent of tetrafluoroethylene and up to 10 mole percent of one or more other comonomers. 55 Other specific polymers which can be used include crystalline copolymers of ethylene and chlorotrifluoroethylene; crystalline copolymers of vinylidene fluoride with one or both of hexafluoropropylene and tetrafluoroethylene, or with 60 hexafluoroisobutylene; and crystalline copolymers of tetrafluoroethylene and hexafluoropropylene. 60

The polymeric composition can optionally contain suitable additives such as pigments, antioxidants, thermal stabilisers, acid acceptors and processing aids. We have found that, although fluorocarbon polymers, in particular ETFE 65 polymers, are recognised in the art to be self-extinguishing, their flammability as 65

measured by the test method described hereinafter is significantly increased by cross-linking according to the invention, but that by including a suitable amount (preferably 0.5 to 6% by weight) of antimony oxide in the composition this potential disadvantage can be substantially removed. It is also possible for the polymeric composition to contain, before step (1) of the process, cross-linking agent which has been added to the polymer before it is shaped, in accordance with the known procedures. However, this is preferably avoided, since the presence of cross-linking agent restricts the conditions which can be used during the shaping step, and in any event tends to produce an extrudate with non-uniform properties along its length. Furthermore, more effective utilisation of the cross-linking agent is obtained when it is imbibed into the shaped article in accordance with the present invention and is not, therefore, subjected to the conditions of the shaping step.

It is also possible for the initial composition to be one which has already been cross-linked, but which requires further cross-linking in order to render the shaped article suitable for its intended use.

The shaped article of the polymeric composition can be of any form. Thus it may be in the form of a sheet, tube or gasket, but it is preferably in the form of a coating on a substrate, particularly an elongate substrate, especially an insulating coating on a metal (e.g. copper) wire or other electrical conductor or on a plurality of parallel spaced-apart conductors. The coating may comprise an inner layer of a first fluorocarbon polymer composition and a second outer layer of a second fluorocarbon polymer composition, the first and second compositions being the same or different. The layers may be in direct contact, either fused together or able to move slightly relative to each other, or they may be joined together by a layer of adhesive.

The shaped article is preferably formed by melt-shaping the polymeric composition e.g. by extrusion, which is preferred, injection moulding or transfer moulding. The temperature at which the composition is melt-shaped is of course above the melting point of the polymer, i.e. above 200°C, and it is often above 250°C. A particularly preferred method is to melt extrude the composition as a coating around an elongate substrate. The fluorocarbon polymer and the method of shaping should be selected so that the shaped article has a tensile strength of at least 3,000 psi (210 kg/cm<sup>2</sup>); and since a higher tensile strength is usually desired in the cross-linked product and there is frequently a loss of tensile strength during the irradiation step, a higher initial tensile strength, e.g. greater than 5,000 psi (210 kg/cm<sup>2</sup>), is preferred. When using crystalline fluorocarbon polymers, and especially when the fluorocarbon polymer is shaped by melt-extrusion as a relatively thin coating, e.g. of thickness up to 0.015 inch (0.04 cm.) around a wire, the initial tensile strength will often be at least 6,000 psi (420 kg/cm<sup>2</sup>), preferably at least 7,000 psi (490 kg/cm<sup>2</sup>), especially at least 7,500 psi (525 kg/cm<sup>2</sup>), particularly at least 8,000 psi (560 kg/cm<sup>2</sup>). Such initial tensile strengths can readily be obtained by known shaping methods.

Preferred cross-linking agents contain carbon-carbon unsaturated groups in a molar percentage greater than 15, especially greater than 20, particularly greater than 25. In many cases the cross-linking agent contains at least two ethylenic double bonds, which may be present, for example, in allyl, methallyl, propargyl or vinyl groups. We have obtained excellent results with cross-linking agents containing at least two allyl groups, especially three or four allyl groups. Particularly preferred cross-linking agents are triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC); other specific cross-linking agents include triallyl trimellitate, triallyl trimesate, tetraallyl pyromellitate, the diallyl ester of 4,4'-dicarboxydiphenyl ether and the diallyl ester of 1,1,3-trimethyl-5-carboxy-3-(*p*-carboxyphenyl)indan. Other cross-linking agents which are known for incorporation into fluorocarbon polymers prior to shaping, for example those disclosed in U.S. Patent Specifications Nos. 3,763,222; 3,840,619; 3,894,118; 3,911,192; 3,970,770; 3,985,716; 3,995,091 and 4,031,167, can also be used. Mixtures of cross-linking agents can of course be used.

The fluid composition comprising the cross-linking agent is preferably a liquid composition; thus the composition may consist essentially of a cross-linking agent having a suitable melting point or be a solution of the agent in an organic solvent, preferably one which is a swelling agent for the polymer. Suitable solvents include chloroform, chlorobenzene, dioxane, trichlorobenzene and many other halogenated or ethereal solvents, e.g. tetrahydrofuran and the dimethyl ether of diethylene glycol. The liquid compositions preferably contain a polymerisation

inhibitor. It is also possible for the agent to be in the form of vapour at atmospheric or superatmospheric pressure.

It is often advantageous for at least part of the contacting of the shaped article and the cross-linking agent to be carried out at an elevated temperature below, preferably at least 25°C below, the melting point of the polymer, for example at least 150°C, preferably 180—225°C, e.g. 180—210°C., since this increases the rate at which the cross-linking agent diffuses into the polymeric composition. When the shaped article is formed by melt-extrusion, the extrudate can be quenched in a liquid composition comprising the cross-linking agent.

The concentration of cross-linking agent at any particular point in the article will of course be dependent on the distance of that point from the surface of the article which is in contact with the fluid composition comprising the cross-linking agent (except in the limiting theoretical case where contacting is continued for so long that equilibrium is achieved). (For the avoidance of doubt it should perhaps be noted that the concentrations of cross-linking agent given herein are average concentrations). Likewise the cross-linking density in the cross-linked article will decrease from the surface to the interior of the article, and it is believed that this may have a useful effect on the physical properties of the article. In order to ensure adequate penetration of the cross-linking agent into the article without excessive contact times, it is preferred that the article should be relatively thin. Thus coatings (which can of course be contacted on only one side) are preferably less than 0.05 inch (0.125 cm) thick, especially less than 0.02 inch (0.05 cm) thick, and self-supporting articles which can be contacted on both sides are preferably less than 0.1 inch (0.25 cm.) thick especially less than 0.04 inch (0.1 cm) thick.

There is often a slow loss of cross-linking agent from the shaped article, for example of 1 or 2%, based on the weight of the article, over a period of a day or more at room temperature, after the article has been removed from contact with the fluid composition. It is, therefore, preferred that the irradiation should be carried out within a few hours at most after completion of the contacting step. At the beginning of step (2) of the first process the shaped article should contain at least 2.5%; preferably at least 4%, especially at least 5%, by weight of the cross-linked agent. Amounts as low as 0.5%, e.g. at least 2%, have an appreciable effect on subsequent cross-linking by irradiation, and can therefore be used in the second process, which involves repeated contacting and irradiation, but in our experience, when cross-linking is effected in a single step, amounts of at least 2.5%, e.g. 4 to 10%, are required in order to obtain products which are substantially superior to those already known. Amounts in excess of 20%, particularly in excess of 30%, seldom lead to results which adequately compensate for the additional time needed in step (1), and often amounts greater than 12% are undesirable. Amounts in the range 5 to 15%, especially 6 to 10%, are preferably employed.

The dosage employed in the irradiation step should be below 50 Mrads to ensure that the polymer is not degraded by excessive irradiation, and the dosages preferably employed will of course depend upon the extent of cross-linking desired, balanced against the tendency of the polymer to be degraded by high doses of irradiation. Suitable dosages are generally in the range 2 to 40 Mrads, for example 2 to 30 Mrads, preferably 3 to 20 Mrads, especially 5 to 25 or 5 to 20 Mrads, particularly 5 to 15 Mrads. The ionising radiation can for example be in the form of accelerated electrons or gamma rays. Irradiation is generally carried out at about room temperature, but higher temperatures can also be used.

The cross-linked articles of the invention have an  $M_{100}$  value of at least 300 psi (21 kg/cm<sup>2</sup>) and a tensile strength of at least 3,000 psi (210 kg/cm<sup>2</sup>), and substantially higher  $M_{100}$  values and tensile strengths are preferred and can readily be obtained, especially when the article is one which has been melt-extruded as a relatively thin article under conditions such that the polymer becomes oriented. Thus the  $M_{100}$  value is preferably at least 450 psi (31.5 kg/cm<sup>2</sup>), particularly at least 600 psi (42 kg/cm<sup>2</sup>), especially at least 750 psi (52.5 kg/cm<sup>2</sup>); and the tensile strength is preferably at least 5,000 psi (350 kg/cm<sup>2</sup>), more preferably at least 6,000 psi (420 kg/cm<sup>2</sup>), particularly at least 7,500 psi (525 kg/cm<sup>2</sup>), most preferably at least 8,000 psi (560 kg/cm<sup>2</sup>). When the shaped article is in the form of an electrically insulating coating on a metal wire, the coating having a thickness of up to 0.015 inch (0.04 cm.), the  $M_{100}$  value is generally at least 450 psi (31.5 kg/cm<sup>2</sup>), preferably at least 500 psi (35 kg/cm<sup>2</sup>), particularly at least 650 psi (45.5 kg/cm<sup>2</sup>), especially at least 750 psi (52.5 kg/cm<sup>2</sup>); and the tensile strength is generally at least 5,000 psi (350 kg/cm<sup>2</sup>), preferably at least 6,000 psi (420 kg/cm<sup>2</sup>), particularly at least 7,000 psi (490 kg/cm<sup>2</sup>), especially at least 7,500 psi (525 kg/cm<sup>2</sup>), most

preferably at least 8,000 psi (560 kg/cm<sup>2</sup>). When the shaped article is in the form of an electrically insulating coating on a metal wire, the coating having a thickness of at least 0.015 inch (0.04 cm.), the  $M_{100}$  value is preferably at least 400 psi (28 kg/cm<sup>2</sup>) and the tensile strength is preferably at least 6,000 psi (420 kg/cm<sup>2</sup>). We have found that when the shaped article is in the form of an insulating coating on a wire, the coated wire shows remarkably high values for resistance to crossed-wire abrasion (a most important characteristic for wires to be used in aircraft), resistance to scrape abrasion, and resistance to high temperature cut-through. For example, insulated wires having crossed-wire abrasion resistances (measured as described below) of at least  $2 \times 10^4$  cycles, and often at least  $2 \times 10^5$  cycles, at 1 kg load, can readily be obtained in accordance with the present invention.

We have also found that insulated wires according to the invention have excellent cut-through resistances, often above 7 lbs. (3.2 kg.) when measured at 150°C by the test described below, especially when the  $M_{100}$  value is at least 750 psi (52.5 kg/cm<sup>2</sup>).

The cross-linked article should have an elongation at least 5%, preferably at least 10%, for most uses, and especially when it is in the form of a coating on a wire, its elongation is preferably at least 40%, particularly at least 50%.

When the shaped article is in the form of a dual-layer coating as described above, contacting with the cross-linking agent can be carried out both before and after the outer layer is applied, using the same or different cross-linking agents, or only after the outer layer has been applied. The contacting is carried out under conditions such that the cross-linking agent is distributing through both layers, so that both layers are cross-linked when exposed to radiation.

The various physical properties referred to in this specification are measured as set out below.

#### $M_{100}$ Values

The  $M_{100}$  values referred to herein are determined by a static modulus test carried out at about 40°C above the melting point of the polymer, (e.g. at about 320°C for the ETFE polymers used in the Examples below). In this test, the stress required to elongate a sample of the cross-linked article by 100% (or to rupture if elongation to 100% cannot be achieved) is measured. Marks separated by 1 inch (2.54 cm) are placed on the centre section of the sample [for example a 4 inch (10 cm) length of insulation slipped off a wire, or a strip  $1/8 \times 0.02 \times 4$  inch ( $0.32 \times 0.05 \times 10$  cm) cut from a slab], and the sample is hung vertically in an oven maintained at the test temperature, with a 2 gm. weight attached to the lower end of the sample. After equilibrating for 2 minutes, the weight attached to the lower end of the sample is increased until the distance between the marks has increased by 100% or the sample breaks. The  $M_{100}$  value is then calculated from the expression

$$M_{100} = \frac{\text{stress} \times 100 + \text{percent elongation}}{\text{Initial cross-sectional area}}$$

#### Tensile Strengths

The tensile strengths referred to herein are determined in accordance with ASTM D638—72 (i.e. at 23°C) at a testing speed of 50 mm (2 inch) per minute.

#### Crossed Wire Abrasion Resistances

The crossed-wire abrasion resistances referred to herein are measured by a test which involves rubbing two crossed wires against each other at a frequency of 50 Hz in a controlled manner, thereby simulating the chafing action that can occur for example in high-vibration areas of aircraft.

The test equipment comprises a small vibrator that is rigidly mounted on a heavy steel frame and causes an axial driver to reciprocate in a horizontal plane. The axial driver is coupled through a horizontal spring steel rod to a rocker arm with a generally horizontal upper surface, on which is mounted a curved wire specimen holder. The centre of the holder is vertically above the centre of rotation of the rocker arm, and its curvature is such that the upper surface of a wire held therein forms an arc of a circle whose center is at the center of rotation of the rocker arm. The radius of the circle is 5.5 inch (14 cm). Therefore, as the wire is displaced horizontally, it does not have any substantial vertical movement.

The second (upper) wire specimen is mounted on the underside of a beam,

one end of which is fastened to the frame through a thin strip of a damping alloy that acts as a hinge and allows the beam to be displaced only in a vertical direction. In the testing position, the beam extends horizontally from the frame so that the wire mounted thereon bears on the wire attached to the rocker arm; the bearing force is provided by a generally vertical rubber band attached to the frame and over the free end of the beam.

The beam and the rocker arm are positioned so that each of the wires forms an angle of 30° with the axis of the axial driver, with an included angle between the crossed wires of 60°. As the lower specimen is reciprocated, the symmetrical arrangement about the driver axis results in a wear pattern that is substantially the same for both wires. The number of cycles needed to cause electrical contact between the wires is measured. The force between the wires is measured with a Hunter force gauge before and after each test by varying a threaded tension adjustment until the upper specimen separates from the lower specimen. A microscope is used to determine the point of separation.

#### Cut Through Resistances

A sample of the wire is laid on an anvil and above the anvil there is a weighted knife blade having a wedge shape with a 90° included angle. The edge of the blade has a 0.005 inch (0.0125 cm.) flat with 0.005 inch (0.0125 cm.) radius edges. The anvil is hung by means of a stirrup from the load cell of an Instron Tensile tester and the knife blade mounted on the movable bar of said Tensile tester so that the blade edge lies transversely over the wire specimen. The knife edge is advanced towards the wire at a speed of 0.2 inches (0.51 cm.) per minute. Failure occurs when the knife edge contacts the conductor. The resulting electrical contact causes the tensile tester to stop advancing the blade. The peak reading from the load cell is taken to be the cut through resistance of the wire.

#### Scrapé Abrasion Resistances

A length of wire is rigidly mounted under tension in a jig and a weighted knife blade having a wedge shape with a 90° included angle and a 0.005 inch (0.0125 cm.) radius at the knife edge is then mounted crosswise to the wire with the knife edge resting on the wire. The knife edge can be loaded with varying weights (3 lbs. (1.36 kg.) in all the examples given) to increase the bearing force of the blade on the wire. To test the scrape abrasion resistance of a given wire the blade is reciprocated with a 2 inch (5.1 cm.) stroke longitudinally along the wire at a frequency of 120 strokes (i.e., 60 cycles) per minute. Failure occurs when the knife edge contacts the conductor, causing an electrical circuit to close.

#### Flammability

The flammability tests were performed in a sheet metal cabinet conforming to FED-STD-191, method 5903 as follows: Two inches (5.1 cm.) of insulation were removed from one end of an 18 inch (46 cm.) specimen and the specimen was mounted vertically under tension with the bared conductor angularly disposed from the vertical so as to enable the Bunsen burner to be mounted vertically directly under the test specimen. A 1.5 inch (3.8 cm.) high yellow flame from a Bunsen burner was applied to the specimen at the junction of the insulation and the bare conductor in such a manner that the lower end of the insulation was located 0.75 inches (1.9 cm.) into the flame. After 12 seconds of flame application, the burner was removed from below the specimen and immediately turned off. The burn length and the time of burning after removal of the flame are recorded. The burn length was the distance from the original bend made in the conductor to the farthest point of damage. Damage is signified by charring of the insulation or baring of the conductor because the insulation has burnt off.

The invention is illustrated by the following Examples and comparative Examples, which are summarised in the Table below, and in which percentages are by weight. In the Table the various symbols have the meanings set out below, and the notation (C) after the Example number indicates that the Example is a Comparative Example [Example 10, marked (C\*), is in itself a Comparative Example, but with Example 11 (and Examples 12 and 13) provides an example of the second process of the invention].

#### Polymers

Polymer A is a mixture of 0.2% TiO<sub>2</sub> and 99.8% of an ETFE polymer ("Tefzel" 280, a polymer sold by E. I. duPont de Nemours and Co. and believed to

contain about 46% ethylene, about 50% tetrafluoroethylene and about 4% of a fluorinated alkenol). Polymer B is the ETFE polymer in Polymer A, without the TiO<sub>2</sub>. Polymer C is a mixture of 0.2% TiO<sub>2</sub>, 4% antimony trioxide and 95.8% of the ETFE polymer in Polymer A. The notations "from 10", "from 11" and "from 12" in Examples 11, 12 and 13 respectively mean that the cross-linked product from the previous Example was used as the starting material. Polymer D is a polymer of ethylene and chlorotrifluoroethylene (1:1 molar) ("Halar" 300 sold by Allied Chemical Co.) Polymer F is an ETFE polymer ("Tefzel" 200, sold by E. I. du Pont de Nemours and Co. and believed to be the same as the ETFE polymer in Polymer A but containing a smaller proportion of the fluorinated alkenol).

#### Cross-linking Agents

TAIC is triallyl isocyanurate.

TAC is triallyl cyanurate.

TATM is triallyl trimesate.

TAPM is tetraallyl pyromellitate.

In Examples 1 to 9, polymeric composition was melt-extruded over a tin-plated copper wire (20 AWG, diameter 0.095 cm.) to form a coating thereon about 0.01 inch (0.025 cms.) thick. In Examples 10 to 13, the polymeric composition was compression-moulded into slabs about 0.01 inch (0.025 cm.) thick, at a mould temperature of 320°C. In Examples 14 to 29, the polymeric composition was melt-extruded into a tape 0.01 inch (0.025 cm. thick). The shaped article was immersed in a bath of the indicated cross-linking agent for the indicated time. The sample was then removed from the bath, excess cross-linking agent was wiped off, and the sample irradiated to the dosage shown. After annealing at 150°C and cooling, measurements were made to ascertain the tensile strength, the M<sub>100</sub> value and the percent increase in weight due adsorption of the cross-linking agent (the percentages in Examples 11—13 being based on the weight of the slab used in Example 10). The article was annealed at 150°C for 1 hour in Examples 1, 8 and 9, for 30 minutes in Examples 2 to 7 and for 15 minutes in Examples 14 to 29; in Examples 10 to 13, the irradiated slabs used for the next Example were not annealed, but the percentage of cross-linking agent, the tensile strength and the M<sub>100</sub> value were determined on a slab annealed at 150°C for 20 minutes.

The insulated wire obtained in Example 1 had the following properties

#### Cut-through Resistance

(a) at 23°C 62 lb. (28 kg.)

(b) at 150°C 7.8 lb. (3.5 kg.)

#### Scrape-abrasion at 23°C:

86 cycles

#### Crossed Wire Abrasion Resistance:

(a) at 2 kg. 4.5×10<sup>5</sup> cycles

(b) at 1.7 kg. 5.4×10<sup>5</sup> cycles

(c) at 1.5 kg 1.8×10<sup>6</sup> cycles

(d) at 1.2 kg. 4.3×10<sup>6</sup> cycles

(e) at 0.8 kg. >3×10<sup>7</sup> cycles

(f) at 0.7 kg. >3×10<sup>7</sup> cycles.

The insulated wires obtained in Examples 2, 3, 4, 5, 6 and 7 have Cut-through Resistances at 150°C of 5.1, 5.9, 6.2, 6.2, 7.1 and 8.2 lb. (2.3, 2.7, 2.8, 2.8, 3.2 and 3.7 kg.) respectively.

The insulated wires obtained in Examples 8 and 9 gave the following results in the Flammability test.

Example No.	Distance Burned inch (cm)	Afterburn (sec)
8	8 (20)	36
9	2 (5)	0

Although the insulation was charred, it did not drip off the wire.

Ex. No.	Polymer	Agent	Temp. °C	Time Mins.	Dose Mrad	TABLE			
						Initial psi (kg/cm <sup>2</sup> )	Final psi (kg/cm <sup>2</sup> )	M <sub>100</sub> psi (kg/cm <sup>2</sup> )	% Wt. increase
1	A	TAIC	203	5	15	>7000 (>490)	8470 (590)	501 (35)	4.5
2 (C)	A	TAIC	200	0.5	8	>6500 (>455)	7200 (500)	200 (14)	1.8
3	A	TAIC	200	2	8	>6500 (>455)	7200 (500)	350 (24.5)	2.9
4	A	TAIC	200	3	8	>6500 (>455)	7200 (500)	458 (32.1)	3.5
5	A	TAIC	200	4	8	>6500 (>455)	7200 (500)	460 (32.1)	4.0
6	A	TAIC	200	5	8	>6500 (>455)	7200 (500)	580 (40.5)	4.9
7	A	TAIC	200	10	8	>6500 (>455)	7200 (500)	800 (56)	7.5
8	A	TAIC	205	2	15	>8000 (>560)	10600 (740)	325 (22.8)	>2.5
9	C	TAIC	205	2	15	>6000 (>360)	7170 (500)	764 (53.5)	>2.5
10 (C*)	B	TAIC	210	1	5	7200 ( 500)	7385 (520)	152 (10.6)	4.9
11	from 10	TAIC	210	2	5	7385 ( 520)	8000 (560)	1360 (95)	13.7
12	from 11	TAIC	210	2	5	8000 ( 560)	7135 (500)	3160 (221)	17.5
13	from 12	TAIC	210	2	5	7135 ( 500)	6000 (420)	6630 (465)	22.0
14	D	TAC	150	30	20	8865 (620)	6422 (450)	641 (44.9)	7.0
15	D	TAC	150	30	50	8865 (620)	*	547 (38.3)	7.0
16	D	TAIC	160	30	20	8865 (620)	7577 (530)	587 (41.1)	5.6
17	D	TAIC	160	30	50	8865 (620)	*	1532 (107.2)	5.6
18	D	TATM	195	60	20	8865 (620)	7665 (536)	961 (67.3)	7.3
19	D	TATM	195	60	50	8865 (620)	6312 (442)	1175 (82.2)	7.3
20	D	TAPM	195	60	20	8865 (620)	6991 (490)	813 (56.9)	5.3
21	D	TAPM	195	60	50	8865 (620)	*	560 (39.2)	5.3
22 (C)	E	TAC	200	10	50	6772 (474)	7102 (497)	264 (18.5)	7.0
23 (C)	E	TAC	200	10	100	6772 (474)	4592 (321)	554 (38.8)	7.0
24	E	TAIC	200	10	50	6772 (474)	5123 (359)	592 (41.4)	9.2
25 (C)	E	TAIC	200	10	100	6772 (474)	*	654 (45.8)	9.2
26 (C)	E	TATM	195	60	50	6772 (474)	6008 (421)	239 (16.7)	2.3
27 (C)	E	TATM	195	60	100	6772 (474)	4914 (344)	252 (17.6)	2.3
28 (C)	E	TAPM	195	60	50	6772 (474)	5083 (356)	162 (11.3)	5.9
29 (C)	E	TAPM	195	60	100	6772 (474)	3200 (224)	272 (19.0)	5.9

\* The sample was too brittle to measure the tensile strength by the method employed, but the tensile strength can be presumed to be greater than 3,000 psi (210 kg/cm<sup>2</sup>).



## WHAT WE CLAIM IS:—

1. A shaped article of a cross-linked polymeric composition wherein the polymer is a fluorocarbon polymer (as hereinbefore defined) having a melting point prior to cross-linking of at least 200°C., the article having an  $M_{100}$  value of at least 300 psi and a tensile strength of at least 3,000 psi. 5
  2. An article according to Claim 1 wherein the shaped article has been prepared by melt-shaping the polymeric composition.
  3. An article according to Claim 1 or 2 which is a coating on a substrate.
  4. An article according to Claim 3 which is an electrically insulating coating on a metal wire. 10
  5. An article according to Claim 4 which is up to 0.015 inch thick and which has an  $M_{100}$  value of at least 450 psi.
  6. An article according to Claim 5 which has an  $M_{100}$  value of at least 500 psi and a tensile strength of at least 6,000 psi.
  7. An article according to Claim 6 which has an  $M_{100}$  value of at least 750 psi. 15
  8. An article according to Claim 6 or 7 which has a tensile strength of at least 8,000 psi.
  9. An article according to Claim 4 which is at least 0.015 inch thick and which has a tensile strength of at least 4,000 psi.
  10. An article according to Claim 9 which has an  $M_{100}$  value of at least 400 psi. 20
  11. An article according to Claim 9 or 10 which has a tensile strength of at least 6,000 psi.
  12. An article according to any one of claims 4 to 11 which has an elongation of at least 50%.
  13. An article according to any one of claims 3 to 12 wherein the article comprises an inner layer of a first said polymeric composition and an outer layer of a second said polymeric composition, the first and second polymeric compositions being the same or different. 25
  14. An article according to any one of claims 1 to 3 which has an  $M_{100}$  value of at least 450 psi and a tensile strength of at least 5,000 psi. 30
  15. An article according to Claim 14 which has an elongation of at least 10%.
  16. An article according to Claim 15 which has an elongation of at least 40%.
  17. An article according to Claim 16 which has an elongation of at least 50%.
  18. An article according to any one of the preceding claims wherein the fluorocarbon polymer contains at least 25% by weight of fluorine. 35
  19. An article according to any one of the preceding claims wherein the fluorocarbon polymer comprises at least 75% by weight of one or more fluorine-containing thermoplastic crystalline polymers, each of which contains at least 25% by weight of fluorine.
  20. An article according to Claim 19 wherein the fluorocarbon polymer comprises up to 15% by weight of a fluorine-containing elastomer or a polyolefin or both. 40
  21. An article according to Claim 19 or 20 wherein the fluorocarbon polymer comprises a copolymer comprising 35 to 60 mole percent of ethylene, 35 to 60 mole percent tetrafluoroethylene and 0 to 10 mole percent of one or more other comonomers. 45
  22. An article according to any one of the preceding claims which contains 0.5 to 6% by weight of antimony oxide.
  23. An insulated wire comprising a metal conductor having an electrically insulating coating thereon of a cross-linked polymeric composition wherein the polymer is a fluorocarbon polymer (as hereinbefore defined) having a melting point prior to cross-linking of at least 200°C, the coating having an  $M_{100}$  value of at least 600 psi and a tensile strength of at least 7,000 psi, and the wire having a crossed wire abrasion resistance as hereinbefore defined of at least  $2 \times 10^4$  cycles at 1 kg. load. 50
  24. An insulated wire according to Claim 23 having a crossed wire abrasion resistance of at least  $2 \times 10^5$  cycles.
  25. An insulated wire according to Claim 23 or 24 wherein the coating has an elongation of at least 50%.
  26. A process for preparing a shaped article as claimed in any one of the preceding claims, which process comprises. 60
- (1) contacting (a) a shaped article of a polymeric composition wherein the polymer is a fluorocarbon polymer (as hereinbefore defined) having a melting point of at least 200°C, the article having a tensile strength of at least 3,000 psi,

with (b) a fluid composition comprising a cross-linking agent, until the article contains at least 2.5% by weight of the cross-linking agent; and

(2) irradiating the shaped article with ionising radiation to a dosage not exceeding 50 Mrads under conditions such that the composition is cross-linked sufficiently to impart thereto an  $M_{100}$  value of at least 300 psi, while maintaining a tensile strength of at least 3,000 psi, the shaped article containing at the commencement of the irradiation P% by weight of the cross-linking agent, where P is at least 2.5%.

27. A process according to Claim 26 wherein the cross-linking agent contains at least two ethylenic double bonds.

28. A process according to Claim 27 wherein the cross-linking agent contains at least two allyl groups.

29. A process according to Claim 28 wherein the cross-linking agent contains 3 or 4 allyl groups.

30. A process according to Claim 28 wherein the cross-linking agent is one or more of triallyl cyanurate, triallyl isocyanurate, triallyl trimellitate, triallyl trimesate, tetraallyl pyromellitate, diallyl diphenyl ether dicarboxylate and the diallyl ester of 1,1,3 - trimethyl - 5 - carboxy - 3 - (*p* - carboxyphenyl) indan.

31. A process according to any one of claims 26 to 30 wherein the fluid composition used in step (1) is a liquid composition.

32. A process according to Claim 31 wherein the liquid composition consists essentially of the cross-linking agent.

33. A process according to Claim 31 wherein the liquid composition is a solution of the cross-linking agent in an organic liquid.

34. A process according to Claim 33 wherein the organic liquid is a swelling agent for the fluorocarbon polymer.

35. A process according to any one of claims 31 to 34 wherein the polymeric composition is shaped by melt-extrusion and the extrudate is quenched in the liquid composition comprising the cross-linking agent.

36. A process according to any one of claims 26 to 30 wherein the fluid composition used in step (1) is a gaseous composition.

37. A process according to any one of claims 26 to 36 wherein the fluid composition is maintained at a temperature of at least 150°C.

38. A process according to any one of claims 26 to 37 wherein the percentage P of the cross-linking agent in the composition at the commencement of irradiation is at least 4%.

39. A process according to Claim 38 wherein P is at least 5%.

40. A process according to any one of claims 26 to 35 wherein P is at most 20%.

41. A process according to Claim 40 wherein P is at most 12%.

42. A process according to Claim 41 wherein P is 6 to 10%.

43. A process according to any one of claims 26 to 42 wherein the shaped article is irradiated to a dosage of 2 to 30 Mrads.

44. A process according to Claim 43 wherein the dosage is 3 to 20 Mrads.

45. A process according to Claim 44 wherein the dosage is 5 to 15 Mrads.

46. A process for preparing a shaped article as defined in any one of claims 1 to 25, which process comprises

(A) contacting (a) a shaped article of a polymeric composition wherein the polymer is a fluorocarbon polymer having a melting point of at least 200°C, the article having a tensile strength at 25°C of at least 3,000 psi (210 kg/cm<sup>2</sup>), with (b) a fluid composition comprising a cross-linking agent, until the article has adsorbed at least 0.5% by weight of the cross-linking agent; and

(B) irradiating the shaped article to a dosage not exceeding 50 Mrads to cause cross-linking thereof while maintaining a tensile strength at 25°C of at least 3,000 psi (210 kg/cm<sup>2</sup>), the shaped article containing at the commencement of the irradiation at least P' % by weight of cross-linking agent absorbed in step (A), where P' is 0.5%; and repeating steps (A) and (B) in sequence until the cross-linked shaped article has an  $M_{100}$  value of at least 300 psi.

47. A process according to Claim 46 wherein P' is at least 2%.

48. A process according to Claim 47 wherein P' is at least 4%.

49. A process according to any one of claims 47 to 50 wherein P' is at most 20%.

50. A process according to any one of claims 46 to 49 wherein the cross-linking agent used in step (A) and the repetitions thereof is as defined in any one of claims 27 to 30.

51. A process according to any one of claims 46 to 50 wherein the fluid composition used in step (A) and the repetitions thereof is as defined in any one of claims 31 to 34.

52. A process according to any one of claims 46 to 51 wherein the same fluid composition is used in step (A) and the repetitions thereof.

53. A process according to any one of the claims 46 to 52 wherein the dosage used in step (B) and the repetitions thereof is 3 to 20 Mrads.

54. A process according to any one of claims 46 to 53 wherein the same conditions are used in step (B) and the repetitions thereof.

55. A process according to Claim 26 substantially as described in any one of the foregoing Examples.

56. A process according to Claim 46 substantially as described in Examples 11 to 13.

57. A shaped article according to any one of claims 1 to 25 when prepared by a process as claimed in any one of claims 26 to 45 and 55.

58. A shaped article according to any one of claims 1 to 25 when prepared by a process as claimed in any one of claims 46 to 54 and 56.

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