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3,081,518

REMOVAL OF STATIC CHARGES

Don R. Carmody, Crete, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana
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This invention relates to the removal or dissipation of static electricity. More particularly, it concerns the dissipation of troublesome electrostatic charges which tend to accumulate on synthetic organic plastics whenever two surfaces are brought into contact with each other.

The versatility and expanding use of synthetic fibers have made almost everyone familiar with their static electricity problems. These range from the inconvenience of clinging, clammy fabrics and the painful sparks obtained from automotive seat covers and floor coverings, through to the serious explosions in hospital operating rooms where anesthetic vapors have been detonated by sparks from surgeons' clothing. In the textile mill, charged fibers jam carding and warping machines and attract dust, causing the textile blemish known as "fog marking." Industrial belting often develops extremely high electrostatic charges which constitute a hazard to personnel.

One method of overcoming these difficulties has been to coat synthetic fabrics with various "anti-static agents," which are usually compounds that impart to the fabric some degree of electrical conductivity. For example, ethylene glycol or polymeric glycol-type materials may be used as coatings to maintain an invisible moisture-absorptive film on fibers. Anti-static agents however tend to collect dust and dirt, and at best are only effective for a limited period because of their removal by dry cleaning, washing, bleaching and wear. It has also been proposed to "ground" fabrics by imbedding metallic wires therein which can be connected to a suitable grounding terminal. While this technique may be used with floor coverings, it is expensive and is obviously of no avail with clothing, automobile seat covers, and the like.

These disadvantages may be completely overcome, according to the present invention, by incorporating directly into synthetic fabrics or other static-susceptible material a bis-cyclopentadiene type compound which contains a radioactive metal isotope. Thus an ionizing radiation of low activity is emitted in the immediate vicinity of the fabric, rendering the surrounding air conductive and thereby dissipating the electrical charges. The bis-cyclopentadienes are extremely stable complexes of various metals with cyclopentadiene and cyclopentadiene derivatives, and may be incorporated in synthetic fabrics by including a bis-cyclopentadiene in the fiber as a solute or plasticizer, by interweaving ordinary synthetic fibers with a minor amount of fibers containing radioactive bis-cyclopentadienes, or, and more preferably, by producing a polymeric fiber having the bis-cyclopentadiene complex as an integral part of the polymer molecule structure. By maintaining radioactive material in close proximity to the electric charges, advantage may be taken of the highly ionizing but short range beta particles as well as the more penetrating gamma radiation. As will appear hereinafter, certain bis-cyclopentadienes are especially suitable for use in such popular but static-susceptible condensation polymers as the polyamides (e.g. "nylon," the polymerized condensation product of adipic acid and hexamethyl-

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ene diamine, and "Perlon," a similar polyamide) and the polyesters (such as "Dacron" and "Terylene" polyesters of terephthalic acid and ethylene glycol), as well as polycarbonates, polyurethanes, etc.

5 Bis-cyclopentadienes, which are stable complexes of polyvalent metals with cyclopentadiene or cyclopentadiene derivatives, have a bis-cyclopentadienyl structure where a single atom of a polyvalent metal is "sandwiched" between two planar cyclopentadiene rings. The earliest complexes were prepared with iron as the central metal atom, and for this reason the generic name "ferrocene" is often given to all compounds having this general structure, whether or not the metal is iron or is ferrous. Thus, 15 bis-cyclopentadienes of the heavy metals scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, ytterbium, zirconium, columbium, molybdenum, ruthenium, rhodium, palladium, most of the rare earths, tantalum, tungsten, iridium, mercury, lead, bismuth and uranium are presently known. Even the metalloids such as arsenic, and the alkaline earth metals magnesium and calcium can form bis-cyclopentadiene complexes. The ferrous group VIII metals iron, cobalt, and nickel, have been most extensively investigated and the radioisotopes thereof are the metals most desirably employed in accordance with the present invention.

25 Bis-cyclopentadienes may be prepared by numerous methods well known to the art; see, for example, the discussion in U.S. Patent 2,804,468. A common procedure utilizes the vapor phase reaction between cyclopentadiene and a metal carbonyl such as iron pentacarbonyl at a temperature within the range of about 250 to about 400° C., followed by recovering the bis-cyclopentadiene product as a solid at lower temperature. Certain bis-cyclopentadienes such as those of iron may be prepared from cyclopentadiene and either a pyrophoric metal oxide or hydrogen gas and a metal oxide. A method of general applicability, and one which is capable of extremely high yields, is the reaction between a cyclopentadiene Grignard and a polyvalent metal chloride. Other processes include the reaction of an alkali metal or alkaline earth metal cyclopentadienyl with a bromide or chloride of the metal which is to be complexed, etc.

35 The resulting bis-cyclopentadiene or dicyclopentadienyl compound, despite its apparent structural resemblance to a cyclic olefin, is in actuality a highly stable aromatic-type material which undergoes many reactions characteristic of aromatic compounds and which does not enter into typical olefin or diolefin reactions such as low temperature bromination or the Diels-Alder adduction. Bis-cyclopentadienes may be alkylated with alkyl or aryl halides by the Friedel-Crafts reaction, they may be condensed with aromatic or aliphatic aldehydes, and may be acylated with acid halides or anhydrides in the presence of acid catalysts. Bis-cyclopentadiene carboxylic acids may be prepared by reacting a bis-cyclopentadiene with an alkali metal hydrocarbon such as n-butyl-lithium, followed by carboxylation with solid carbon dioxide and acidification with hydrochloric acid. In general, only one position on each cyclopentadiene ring enters into a substitution reaction, although bis-cyclopentadienes having more than one substituent on each ring may be prepared from the corresponding poly-substituted cyclopentadiene. The foregoing methods are of general applicability to bis-cyclopentadienes, and may be employed in the manufac-

ture of various radioactive bis-cyclopentadiene compounds which may either be employed as radioactive plasticizer-type additives or which may be caused to react with synthetic polymers and become an integral constituent of the fiber molecule.

Several alternative techniques are available for obtaining bis-cyclopentadiene complexes or radioactive metal isotopes. For example, a bis-cyclopentadiene may be prepared from a non-radioactive metal, and the complex may thereafter be subjected to neutron bombardment in an atomic pile. Another method, and one which is less likely to cause degradation of the cyclopentadiene ring, is to prepare the complex from a metal which is initially radioactive. This latter procedure offers the additional advantage of offering convenient control over the amount of radioactivity in the final product. Either of these two methods however is preferable to subjecting the finished synthetic fiber to neutronic bombardment unless for other reasons it is desired to subject the finished material to irradiation. This may be the case with hydrocarbon polymers such as polyethylene where certain properties of the base polymer are improved by such treatment.

As indicated previously, it is preferred to incorporate the radioactive bis-cyclopentadiene complex into synthetic polymers by actually forming a polymer having the complex as an integral part of the polymeric molecule structure. For example, monovinyl or divinyl dicyclopentadienyl iron may be co-polymerized with such materials as methyl methacrylate, styrene, or chloroprene, as well as with other olefinically unsaturated monomers following the method of Arimoto and Haven, J.A.C.S., 77, pp. 6295-7, 1955. The monovinyl monomer may be prepared by acetylating dicyclopentadienyl iron with acetic anhydride, followed by reduction to the alcohol with lithium aluminum hydride, and pyrolysis of either the alcohol or an acetate ester to the vinyl compound. Monovinyl bis-cyclopentadiene (iron) homopolymers are also known, and, in accordance with one aspect of the invention, the homopolymer may contain a relatively small number of ferrocene molecules having radioactive metals included therein for static electricity dissipation. Depending upon the polymerization catalyst used, monovinyl cyclopentadiene (iron) polymers may be obtained in the form of oils (persulfate catalyst), viscous oils (phosphoric acid catalyst), or high melting solids (azodisobutyronitrile catalyst).

Where the synthetic polymer is of the polyamide ("nylon") or the polyester ("Dacron") type, the preferred ferrocene derivative is the bis-cyclopentadiene carboxylic acid, preferably the dicarboxylic acid, or esters thereof. Monocarboxylic acids form the end of a polymer chain, while dicarboxylic acids enter into the central portion. Bis-cyclopentadiene carboxylic acids enter into polycondensation reactions as esters in the same manner as the aliphatic or aromatic dicarboxylic acids normally used in preparing the fibers. As illustrative examples, a small amount of iron-59-containing bis-cyclopentadiene dicarboxylic acid may be added to the adipic acid and hexamethylenediamine which are thereafter heated under pressure to form a nylon salt solution, which is then polymerized and extruded in known manner to nylon staples of commerce (see, for example, Shreve, "Chemical Process Industries," pages 734-736, 1945). Alternately, the radioactive bis-cyclopentadiene dicarboxylic acid may be added to the nylon salt after reaction of adipic acid with hexamethylenediamine and before polymerization. As applied to polyester fibers such as polyethylene glycol terephthalate, the fiber is conventionally produced by conducting an ester interchange reaction between dimethyl terephthalate and ethylene glycol to form bis-glycol terephthalate, followed by polycondensation at high temperature and high vacuum to a linear polyester (Whinfield and Dickson, U.S. Patent 2,465,319). As is the case with polyamides, the radioactive bis-cyclopenta-

diene complex may be introduced at any stage of the manufacturing process.

In synthetic polymers where it is inconvenient to incorporate the complex directly in the polymer structure, and in certain instances where this may be possible but undesirable, the radioactive complex may be simply admixed with, or impregnated into, the polymer while in the form of a chemically stable bis-cyclopentadiene or substituted bis-cyclopentadiene. This procedure is of particular merit with ethylene and propylene homopolymers and copolymers. For example, the lower alkyl esters of bis-cyclopentadiene carboxylic and bis-cyclopentadiene dicarboxylic acids are soluble in organic solvents and are thus readily introduced into organic solutions of various polymers or monomers, yet they are substantially completely insoluble in water and hence resist extraction from the final fiber product. Similarly, the alkyl substituted bis-cyclopentadienes (which may be prepared by zinc-HCl reduction of ketones of the several bis-cyclopentadienes, Nesmeynov, et al., Doklady Akad. Nauk SSSR, 107, pages 262-64, 1956) such as ethyl bis-cyclopentadiene, diethyl bis-cyclopentadiene, dipropyl bis-cyclopentadiene, and dibutyl bis-cyclopentadiene are excellent plasticizers as they are fairly soluble in aromatics and in aliphatics, sparsely soluble in polar organics, and are quite insoluble in water.

The amount of radioisotope which is to be used may vary over wide ranges depending upon the particular application of the fabric. If a fiber is to be used in contact with people, the safe amount of irradiation must be limited to 12.5 milliroentgens per hour, which is approximately equivalent to the production of 10^9 ion pairs per hour in air. In applications where direct personal contact is unlikely, such as for example in industrial belting and in reinforcing fibers for gasoline filling station hoses, substantially more concentrated radioactivity is desirable and may be employed. Since 32.5 electron volts of energy are required to form one ion pair, the radioactive isotope must have a radiant energy which exceeds this limit, and in this respect such isotopes as iron-59, cobalt-60, nickel-63 and thallium 204, as well as many other isotopes, are suitable. Cobalt-60, nickel-63 and thallium 204 however have quite long half lives, and thus provide static electricity dissipation over substantially longer periods than with radioisotopes of short half lives. Isotopes which are especially suitable are those which have a strong beta particle emission, for the reason that these particles are more effective in ionizing air than are gamma rays.

As a specific example of a static-free fabric, polyethylene terephthalate fibers may be interspersed with fibers consisting essentially of cobalt bis-cyclopentadiene polyester which contains about 0.1 millicurie of cobalt-60 per gram of fiber, in a ratio such that the resulting fabric generates about 10^9 ion pairs in air per square yard of fabric per hour. Such fabric is suitable for personal wear and will remain essentially free of static charges for the life of the fabric. Cobalt-60 may be prepared by subjecting non-radioactive cobalt-59 metal or oxide to pile radiation. A typical pile neutron flux of 5×10^{11} neutrons/cm.²/sec. for 28 days will produce a specific activity of about 47 millicuries per gram of total cobalt.

The following tabulation suggests several suitable artificial radioisotopes which are currently available and which may be employed for use in accordance with the invention. These isotopes are prepared by pile irradiation, as fission fragments from spent nuclear reactor fuel elements, by cyclotron bombardment, etc., and may be employed singly or in admixture. The criterion of selection for the table was that the radioisotope should desirably have a half life of more than about 28 days and not more than about 85 years, more desirably not more than about 10 years. It will be appreciated however that isotopes with longer or with shorter half lives may be employed but with somewhat more difficulty in securing

or maintaining adequate radioactivity. Radioactive daughters are in parentheses.

Radioisotope	Half life	Radiation
Calcium-45	163 days	Beta.
Scandium-46	85 days	Beta, Gamma.
Chromium-51	28 days	Gamma.
Cobalt-58	72 days	Beta+, Gamma.
Iron-59	45 days	Beta, Gamma.
Cobalt-60	5.3 years	Beta, Gamma.
Nickel-63	25 years	Beta.
Strontium-90 (Yt-90)	65 years	Beta.
Zirconium-95 (Nb-95)	65 days	Beta, Gamma.
Ruthenium-106 (Rh-106)	1.0 year	Beta, Gamma.
Barium-133	9.5 years	Gamma.
Cerium-141	32 days	Beta, Gamma.
Cerium-144 (Pr-144)	282 days	Beta, Gamma.
Promethium-147	2.6 years	Beta.
Europium-152-154	13-16 years	Beta, Gamma.
Tantalum-182	115 days	Beta, Gamma.
Tungsten-185	73 days	Beta.
Iridium-192	74 days	Beta, Gamma.
Mercury-203	45 days	Beta, Gamma.
Thallium-204	4 years	Beta.

From the foregoing it is clear that the present invention provides an extremely satisfactory method of dissipating the static electricity which is particularly troublesome when employing synthetic fiber fabrics. By incorporating a small amount of bis-cyclopentadiene material containing a radioisotope, the fiber may be permanently rendered static free. As a result, synthetic fibers which heretofore jammed carding and warping machines and which caused "fog marking" of textiles need no longer be problems in the mill, and users of such fabrics need no longer be troubled with clinging fabrics and sparking auto seat covers and rugs. In addition, the treatment is essentially permanent, and resists continued wear and repeated dry cleaning and washing.

I claim:

1. A synthetic organic polymer fabric normally tending in use to accumulate static electricity charges and containing, in an amount effective to at least partially dissipate such charges, a bis-cyclopentadiene type complex of a radioactive polyvalent metal isotope.

2. The fabric of claim 1 wherein said bis-cyclopentadiene type complex is an integral part of the polymer molecule structure.

3. The fabric of claim 1 wherein said bis-cyclopentadiene type complex is present as a plasticizer.

4. The fabric of claim 1 wherein said bis-cyclopentadiene type complex is contained in a minor amount of fibers interwoven in said fabric.

5. The fabric of claim 1 wherein said organic polymer is a polyester.

6. The fabric of claim 1 wherein said organic polymer is a polyamide.

7. The fabric of claim 1 wherein said organic polymer is a polyolefin.

8. The fabric of claim 1 wherein said radioactive polyvalent metal isotope has a half life between from about 28 days to about 85 years.

9. A synthetic organic polymer fiber normally tending in use to accumulate static electricity charges and containing, in an amount effective to at least partially dissipate such charges, a bis-cyclopentadiene complex of a radioactive polyvalent metal isotope.

10. The fiber of claim 1 wherein said radioactive polyvalent metal isotope comprises cobalt-60.

11. The fiber of claim 1 wherein said radioactive polyvalent metal isotope comprises nickel-63.

12. The fiber of claim 1 wherein said radioactive polyvalent metal isotope comprises iron-59.

13. The fiber of claim 1 wherein said radioactive polyvalent metal isotope comprises thallium-204.

14. The fiber of claim 1 wherein said radioactive polyvalent metal isotope comprises strontium-90.

15. A process for imparting the property of static electricity charge dissipation to a material normally tending in use to accumulate such charges, which process comprises incorporating in said static-electricity-accumulating material a bis-cyclopentadiene complex of a radioactive polyvalent metal isotope, whereby the surrounding atmosphere is ionized and rendered electrically conductive.

16. The process of claim 15 wherein said radioactive polyvalent metal isotope has a half life of from about 28 days to about 85 years.

17. The process of claim 16 wherein said radioactive polyvalent metal isotope is radioactive isotope of a ferrous group VIII metal.

18. The process of claim 15 wherein said material is a synthetic organic polymer fabric.

19. A process for dissipating static electricity charges from a material normally tending in use to accumulate such charges, which process comprises ionizing the surrounding atmosphere by means of an ionizing radiation emitted from a radioactive polyvalent metal isotope contained in a bis-cyclopentadiene complex.

References Cited in the file of this patent

UNITED STATES PATENTS

1,154,127	Rasehorn et al. -----	Sept. 21, 1915
1,956,948	Fattinger et al. -----	May 1, 1934
1,980,519	Grunzig et al. -----	Nov. 13, 1934
2,166,740	Karplus -----	July 18, 1939
2,169,657	Millson -----	Aug. 15, 1939
2,412,126	Conrad -----	Dec. 3, 1946
2,428,046	Sisson et al. -----	Sept. 30, 1947
2,501,435	Caspé -----	Mar. 21, 1950
2,562,138	Bump et al. -----	July 24, 1951
2,587,505	Moody -----	Feb. 26, 1952
2,630,620	Rand -----	Mar. 10, 1953
2,722,730	Knowland et al. -----	Nov. 8, 1955

OTHER REFERENCES

"Industrial Applications of Radioactivity," Electronics, April 1948, pages 78 and 79 relied on.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,081,518

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Don R. Carmody

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 6, 8, 10, 12 and 14, for the claim reference numeral "1", each occurrence, read -- 9 --.

Signed and sealed this 8th day of October 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWIN L. REYNOLDS
Acting Commissioner of Patents