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AIRSHIP ENVELOPES

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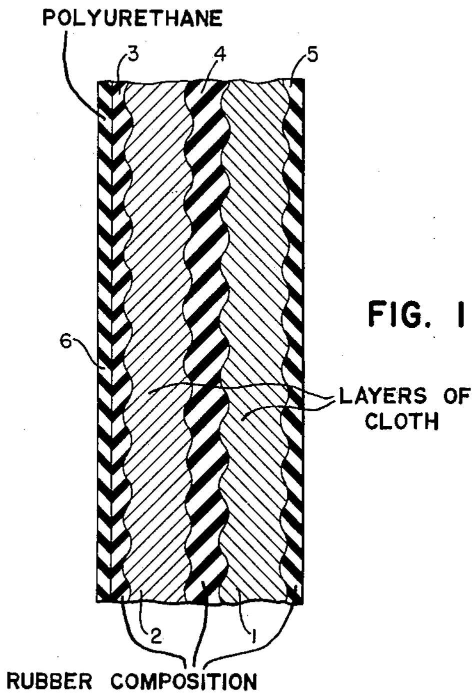

FIG. 1

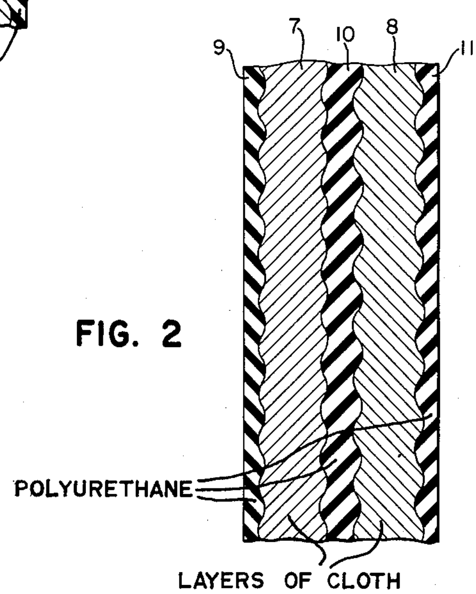

FIG. 2

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AIRSHIP ENVELOPES
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This invention relates to airships of the lighter-than-air type. More particularly, it relates to improved outer covers or envelopes for airships, to methods for preparing these improved covers and to methods for repairing the outer covers of airships while in service.

The outer cover or envelopes for airships are prepared by coating a cloth or fabric, such as rayon, cotton, nylon or dacron, on both sides with a rubber composition, plying-up two such coated fabric layers so that the warp of one layer is at an approximate 45° angle to the warp of the other layer to aid in providing dimensional stability in the envelope, curing the plied-up assembly, cutting patterns from the cured laminate, buffing the rubber from the edges of the cut patterns, cementing the buffed edges, sewing the cut patterns to form the desired envelope shape, taping the sewn seams and applying an exterior paint to the finished envelope.

Since the envelope is the container for the helium gas conventionally employed to provide the lift to the airship, it is necessary that the envelope be as nearly gas-tight and diffusion-resistant as possible. It has been observed that even when the airship envelopes are coated with rubber having outstanding resistance to diffusion, the airships after being in service for some time lose helium through leakage or diffusion at such a rate that the effective lift of the aircraft is seriously reduced. Also, the air diffusing into the envelope increases the density of the gas. This air can be removed only by an expensive and time-consuming purification operation or by removing the impure helium gas and re-inflating with purer helium. One solution to this leakage and diffusion problem is to increase the thickness of rubber coating employed on the envelope fabric. This, however, increases the dead weight in the airship and reduces its effective lift.

It is, therefore, an object of this invention to provide coatings for airship envelopes. Another object is to prepare airship envelopes from these improved coatings without increasing the dead weight of the airship. Another object is to provide envelopes for airships which have a minimum weight amount of coating composition consistent with maximum resistance to leakage and diffusion. Still anothetr object is to repair the envelopes of airships in service without the removal of the envelope from the airship. Another object is to reduce the amount of diffusion and leakage of helium gas in airship envelopes so that the requirement for purifying the contained helium gas will be minimized. Other objects will appear as the description proceeds.

The objects of this invention are accomplished by employing as the coating for airship envelope fabric, either in the manufacture of new envelopes or the repair of existing envelopes, a reaction product of a polyisocyanate and an active-hydrogen-containing polymeric material such as a polyester, polyether or polyesteramide.

The practice of this invention is illustrated with respect to the accompanying drawings in which FIG. 1 and FIG. 2 are sectons of airship envelope constructions. FIG. 1 shows two plies **1** and **2** of cloth coated with layers **3**, **4** and **5** of rubber composition. In this particular embodiment of this invention a layer **6** of the reaction product of a polyisocyanate and an active-hydrogen containing polymeric material is applied over the outer layer **3** of

rubber. This outermost layer **6** may be applied to the envelope as originally fabricated or it may be applied at any time the gas-retaining properties of the envelope fall below the degree required for satisfactory service of the airship. FIG. 2 shows an airship envelope comprising two plies **7** and **8** of cloth coated with layers **9**, **10**, and **11** of a composition containing a polyisocyanate and an active-hydrogen-containing polymeric material. In this embodiment of the invention the excellent diffusion and weathering properties of the reaction mixture are taken full advantage of, since this type of material represents the only rubber-like material present in the airship envelope.

Examples of the active-hydrogen-containing polymeric materials useful in preparing the reaction product used to coat the airship envelopes are polyesters, polyesteramides, polyalkylene ether glycols and mixtures of two or more of these. By the term "active-hydrogen" used to describe these polymeric materials is meant those hydrogen atoms which are reactive as measured and determined by the Zerewitinoff method. The polyesters are prepared by the condensation reaction between one or more glycols and one or more dibasic carboxylic acids. The polyesteramides are prepared from one or more glycols, one or more dibasic carboxylic acids and relatively small amounts of one or more bifunctional amino-bearing compounds such as amino carboxylic acids, amino alcohols, or diamines. Small amounts of trifunctional materials may optionally be employed in preparing the active-hydrogen-containing polyesters and polyesteramides. The polyalkylene ether glycols are hydroxyl-terminated polyethers derived from gylcols or alkylene oxides or from other heterocyclic ethers such as dioxolane. Further examples of these active-hydrogen-containing polymeric materials and methods for their preparation are described in United States Patents 2,625,531; 2,625,532; 2,625,535 which show polyesters and polyesteramides and United States Patents 2,692,873 and 2,702,797 which show the polyalkylene ether glycols. Preferred active-hydrogen-containing polymeric materials are the polyethers having an average molecular weight of from approximately 1,000 to 5,000, and polyesters of similar molecular weight having an acid number not greater than 5. Best results are obtained with the hydroxyl-terminated polyethers having an average molecular weight of approximately 2,000.

The polyesters, polyethers and polyesteramides of average molecular weight between 1,000 and 5,000 are either liquid at room temperature or capable of being melted at relatively low temperatures. They are transformed by reaction with polyisocyanate into solid cured materials. In such liquid form they can be applied in admixture with polyisocyanates and other compounding ingredients, directly to the outer surface of an already-formed airship envelope by painting or spraying, for instance. Also such liquid mixtures may be painted or spread upon the plies of fabric employed to fabricate the airship envelope. It is desirable to add a solvent such as methyl isobutyl ketone to the polymer/poylisocyanate reaction mixture to provide the consistency desired for most efficient application to the fabric or airship envelope. To save time in the curing of the coating after it is applied, it it preferred to form a liquid prepolymer of the polyester or polyether and polyisocyanate before applying it to the fabric. These prepolymers are conveniently prepared by adding approximately two mols of diisocyanate to one mol of polyester or polyether and heating the mixture, in the presence or absence of solvents, for approximately ten hours at 175° F.

It is possible to produce from polyethers, as well as from polyesters and polyesteramides, uncured elastomeric products similar in physical state to unvulcanized natural rubber by controlling the extent of reaction between the polyether and the polyisocyanate.

Methods for preparing this solid uncured elastomer are described in the patents referred to above. These solid uncured elastomers are also useful in the practice of this invention by mixing them with the curing agent, such as additional polyisocyanate, and other conventional compounding ingredients, and spreading the compounded uncured elastomer onto the fabric in cement form or calendering such compounded elastomers onto the layer of fabric. This solid form of the reaction product may also be used in the outer cover coating of new airships or for repairing the envelopes of airships already in service by making a paint or cement of the elastomer and a solvent. Conventional solvents such as methyl ethyl ketone or dimethyl formamide may be employed to make the cement for spreading or painting purposes. It is also possible to apply the uncured elastomeric material to the fabric in the form of a melt formed by heating the material sufficiently to reduce it to a flowable consistency.

Of the various physical forms in which the coating can be applied to the fabric or envelope and the various methods of preparing the coating composition, a particularly effective coating composition is one prepared in the form of a cement or paint containing approximately 35% by weight of a prepolymer of polyether/polyisocyanate, for instance, and approximately 65% by weight of solvent. This weight ratio of solids to solvent provides a solution which is readily flowable and easily applied to the fabric by painting.

Any polyisocyanate, and preferably a diisocyanate may be employed in these coating compositions. Representative examples of such polyisocyanates are the meta-tolylene diisocyanates such as 2,4 and 2,6-tolylene diisocyanate or mixtures of these; 4,4-diphenyl methane diisocyanate; 4,4′-diphenyl diisocyanate; 1,5-naphthalene diisocyanate; 3,3′-dimethyl 4,4′-diisocyanato diphenyl; 3,3′-dimethoxy 4,4′-diisocyanato diphenyl; 3,3′-dimethyl 4,4′-diisocyanato diphenyl methane and mixtures of diisocyanates and higher functional polyisocyanates such as those described in United States Patent 2,683,730.

To the reaction mixture of polyisocyanate and the active-hydrogen-containing polymeric material, may be added compounding ingredients useful in the preparation of the fabric coating composition. These useful ingredients include catalysts, and a metallic powder or flake, such as aluminum flake, for coatings which are to be applied to the outer surface of the airship envelopes. Specific catalysts which are useful in accelerating cure of the coating composition are the tertiary amines, such as N-methyl morpholine and the condensation products of aldehydes and amines, such as the condensation product of approximately 4 mols of butyraldehyde and one mol of aniline similar to those described in The Journal of American Chemical Society, vol. 70, page 1624 for April 1948. The metallic powders employed in outer surface coating aid in the weathering resistance of the coating itself and provide a reflective surface which maintains the helium gas enclosed in the envelopes at a lower temperature. A suitable metallic powder for the purpose is Alcoa aluminum powder #422.

Any of the natural or synthetic rubbers may be employed in coating the fabric layers of the airship envelope which is subsequently to be coated on its outer surface with the polymer/polyisocyanate coating. Examples of these rubbers are natural rubber, the rubberlike copolymers of butadine and styrene, the copolymers of a major proportion of an iso-olefin and a minor proportion of a di-olefin, known as butyl rubber, and the polymers of 2-chlorobutadiene-1,3, known as polychloroprene or neoprene. Of these rubbers, neoprene is preferred because of its resistance to weathering and its high resistance to diffusion.

Other rubbers which can be advantageously employed in coating fabric for airship envelopes are the mercaptan-

modified polymers described in copending application Serial No. 543,360 filed October 28, 1955, now abandoned. As described therein, these rubbers are prepared by reacting at least one aliphatic mono-mercaptan containing from 1 to 6 carbon atoms, such as methyl mercaptan, with at least one synthetic rubber latex containing a polymer selected from the group consisting of emulsion-polymerized conjugated diolefins containing from 4 to 6 carbon atoms, such as polybutadiene, and emulsion-polymerized copolymers of at least one conjugated diolefin containing from 4 to 6 carbon atoms with up to an equal amount by weight of at least one monomer containing a reactive component selected from the group consisting of vinyl and vinylidene radicals polymerizable with said diolefin, the double bonds present in said polymer being saturated by reaction with the mercaptan to the extent of at least 30% of the total double bonds present in said polymer, the mercaptan/polymer addition product having a Mooney plasticity, as measured by the large rotor at 212° F. of not less than 35. For airship envelope construction a methyl mercaptan modified polybutadiene saturated to the extent of from 80 to 95% of the double bonds is particularly useful. This type of rubber is lower in specific gravity than neoprene and has outstanding resistance to diffusion as well as excellent resistance to oxidation, sunlight, and ozone, which properties make it particularly attractive for airship envelope construction.

The practice of this invention is further illustrated with respect to the following examples which are representative rather than restrictive of the scope of this invention. Parts are shown by weight unless otherwise specified.

EXAMPLE I

A prepolymer was prepared by reacting, in 34 parts of ethyl acetate solvent, 16.4 parts of tolylene diisocyanate with 85 parts of a polyester prepared from the condensation reaction between adipic acid and 33.3 mol percent of ethylene glycol and 33.3 mol percent of diethylene glycol and 33.3 mol percent of 1,4-butane diol. This polyester had a hydroxyl number of approximately 60, an acid number of about 1.0 and an average molecular weight of approximately 1850. The prepolymer was prepared by reacting the polyester/diisocyanate mixture for approximately 10 hours at 175 degrees F. This prepolymer was then dissolved in methyl isobutyl ketone to a solids content of about 35%. Based upon 100 parts of prepolymer in solution the following ingredients were added to the prepolymer solution just before it was to be applied to the outer surface of an airship envelope.

8.8 parts of meta tolylene diisocyanate
22.7 parts of aluminum powder (Alcoa #422)
2.0 parts of a 10% solution in toluene of an accelerator prepared by condensing butyraldehyde with aniline.

An airship, originally charged with 99.5% pure helium, had after one year of service lost helium through leakage and diffusion to such an extent that the percentage of helium purity in the airship had been reduced to 87.2%. The polyester/diisocyanate mixture prepared according to Example I was applied to the envelope of this airship, and the helium content of the airship was purged to provide a new helium purity of 96.2%. After seven months of service with the polyester/diisocyanate coating functioning as a diffusion-resistant barrier, further determinations showed that there was no measurable loss in helium purity.

EXAMPLE II

A prepolymer was prepared by reacting 153.7 parts of polypropylene ether glycol of approximately 1025 molecular weight with 52.2 parts of meta-tolylene diisocyanate for 3 to 4 hours at 80–90° C. This prepolymer (30 parts) was then dissolved in 16,3 parts of methyl isobutyl ketone and 65.3 parts of xylene. Before the solution was to be applied to the airship envelope, 2.5 parts of a 10% solution in toluene of an accelerator prepared by condensing butyraldehyde with aniline, 2.0 parts of metatolylene diisocyanate and 6.4 parts of aluminum flake were added to the prepolymer solution.

The coating compositions prepared according to Examples I and II have outstanding resistance to diffusion and excellent resistance to weathering. As coatings for airship envelope construction or repair they provide for relatively trouble-free service and maximum protection against loss of lift in the airships consistant with minimum added dead weight. Other coating compositions may be prepared as described in Examples I and II employing other diisocyanates, other polyester, polyethers, or polyesteramides, other accelerators and other compounding ingredients as disclosed above. Such coating compositions may be employed either to fabricate an entire airship envelope, to coat the outer surface of a new airship envelope, or to repair airship envelopes after they have been in service.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

We claim:

1. An airship envelope comprising a plurality of layers of fabric coated with a vulcanized rubber composition which is covered contiguously on its outermost surface with a reaction product of a polyisocyanate and an active-hydrogen-containing polymeric material selected from the group consisting of polyesters, polyethers and polyesteramides having an average molecular weight of from 1,000 to 5,000 and an acid number not greater than 5, said reaction product being in direct contact with said envelope, said vulcanized rubber composition comprises the elastomeric addition product of

(A) at least one aliphatic mono-mercaptan having from 1 to 6 carbon atoms and

(B) at least one synthetic rubber latex containing an emulsion polymerized polymer of at least one conjugated diolefin having from 4 to 6 carbon atoms with from none to an equal amount by weight of at least one monomer containing a reactive component selected from the group consisting of vinyl and vinylidene radicals which are polymerizable with said diolefin,

in which the double bonds present in the polymer are saturated by reaction with the mercaptan to the extent of at least 30% of the total double bonds present in said polymer, said addition product having a Mooney plasticity (large rotor) or not less than 35.

2. An airship envelope defined by claim 1 in which the active-hydrogen-containing polymeric material is a polyether.

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