STRESS CRACK RESISTANT SEALANT

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26 August 1974
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ABSTRACT OF THE DISCLOSURE

A sprayable material for aircraft skin fastener head areas is formed from a fully saturated prepolymer that is a reaction product of polytetramethylene ether glycol and 2,4 toluene di-isocyanate. The prepolymer is mixed with toluene to form a first mixture. This first mixture is combined with a second mixture of 4,4' methylene-bis-2-chloroaniline and urethane grade methyl ethyl ketone. The sprayable material is applied over an epoxy-polyamide primer coating covered by a metal pretreatment coating compound. An aliphatic polyurethane coating is then applied over the sprayable material.

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

The present invention generally relates to protective coatings for surfaces and more particularly to coatings for the protection of aircraft skin fastener head areas.

Various materials have been used heretofore to protect aircraft and other surfaces from the corrosive effect of extreme atmospheric and weather conditions. In accordance with one such method, a polysulfide rubber sealant is applied as a stress absorbing coating to prevent cracking around fastener
heads during flight operations. One of the deficiencies of polysulfide sealants, however, is their inability to withstand even short term heating above 225° F. The F-14A aircraft, which will become operational in the not too distant future, will experience frictional skin heating up to 325° F for short periods of time. An improved sealant will therefore be required for this aircraft.

Neoprene and other conventional coatings have been found to possess difficult application characteristics, moderate to poor resistance to radiant heat, poor resistance to diester type aircraft lubricants, and/or inadequate resistance to rain erosion. In addition, the neoprene and other conventional coatings suffer severe flight stress degradation and are likely to crack particularly in the aircraft skin fastener head areas, thereby exposing the aircraft to corrosive effects.

**SUMMARY OF THE INVENTION**

Accordingly, it is a general purpose and object of the present invention to provide improved protection for aircraft and other structural surfaces against erosion for prolonged intervals. It is a further object to provide a method of protecting these surfaces with applied materials that are applied in a minimum number of coatings and are particularly resistant to cracking from flight stress in the aircraft skin fastener head areas. Additional objects are that the applied materials have easy application characteristics and are resistant to radiant heat, aircraft lubricants and rain erosion.

This is accomplished according to the present invention by providing a unique stress resistant coating composition adapted for use with other coating compositions on the aircraft.
or other structural surface to be protected. The stress resistant coating is comprised of a first mixture polyurethane prepolymer and toluene, and a second mixture of 4,4'-methylene-bis-2-chloroaniline and methyl ethyl ketone (urethane grade). The stress resistant coating is adapted for use as a spray and is applied to a surface over an epoxy primer and pretreatment coating. An aliphatic polyurethane coating is then applied over the stress resistant coating.

**DESCRIPTION OF THE PREFERRED EMBODIMENT**

A sprayable coating composition suitable for application on the surface of an aircraft or other structural surface is prepared by first intimately admixing a polyurethane prepolymer which is known in the art as Adiprene L-100 (duPont), a second polyurethane prepolymer known as Adiprene L-42 (duPont) and toluene in a closed pebble mill. Adiprene L-100 (duPont) is the reaction product of polytetramethylene ether glycol and 2,4 toluene di-isocyanate has an average molecular weight of approximately 2000 and contains 4 to 4.3% isocyanate by weight. Adiprene L-42 (duPont) is the reaction product of polytetramethylene ether glycol and 2,4 toluene di-isocyanate has an average molecular weight of approximately 2000 and contains 2.7 to 2.9 isocyanate by weight. Although both Adiprene L-100 and L-42 (duPont) are known to be effective abrasion resistant material, they are generally available and used individually in 100% solid form. Prior to use, each must be mixed and applied at 212° F. In addition, each has a relatively short pot life of only a few minutes. The toluene in the present invention is used to thin the polyurethane prepolymer so that they can later be more easily and effectively applied to the surface to be protected. The polyurethane prepolymer...
as well as the toluene solvent are necessarily carefully kept
in an anhydrous condition so as to maintain the stability of
the coating composition prior to its application to the surface
to be protected. The thinned polyurethane prepolymer is then
cured with a mixture of 4,4'-methylene-bis-2-chloroaniline and
methyl ethyl ketone (urethane grade). The chemical structural
formula of the 4,4'-methylene-bis-2-chloroaniline is:

\[ \text{HN} \quad -\text{C} = \text{C} - \text{NH}_2 \]

The sprayable coating composition is applied over an
epoxy primer and pretreatment coating to the fastener head
areas of an aircraft or other surface to be coated. An aliphatic
polyurethane can then be applied over the sprayable coating
composition. The sprayable coating composition in addition
to be sprayed may be applied by brushing or any other suitable
mode of application. Application of the sprayable coating
composition can be performed satisfactorily at ambient
temperature and pressure conditions even at very high humidities.
The composition after being applied is allowed, preferably at
least one week, to complete the curing operation.

The following examples are intended to illustrate the
invention but not to limit it in any way.

**Example 1**

10.9 parts by weight of a first fully saturated urethane
prepolymer which is known as Adiprene L-100 (DuPont) and
which is a reaction product of polytetramethylene ether glycol
and 2,4 toluene di-isocyanate having an average molecular
weight of approximately 2000 and containing 4 to 4.5% of iso-
cyanate groups by weight, was ground in a closed pebble mill
with 43.6 parts by weight of a second fully saturated urethane prepolymer which is known as Adiprene L-42 (DuPont) and 54.0 parts by weight of toluene to form a suspension. The second prepolymer is a reaction product of polytetramethylene ether glycol and 2,4 toluene di-isocyanate having an average molecular weight of approximately 2000 and containing 2.7 to 2.9% of isocyanate groups by weight. The toluene prior to use had been dried over sodium. Two volumes of the resulting suspension were then mixed with one volume of a curing agent which consisted of 5.2 parts by weight of 4,4' ethylene-bis-2-chloroaniline and 33.9 parts by weight of methyl ethyl ketone (urethane grade). The resulting formulation was then applied to a MIL-C-5541 aluminum alloy fatigue assembly having cadmium plated fasteners over one coat of MIL-L-23377 epoxy primer of a thickness of from 0.6 - 0.9 mils (1 hour dry), and one coat MIL-C-8514 pretreatment coating of a thickness of from 0.3 - 0.5 mils (1 hour dry). The resulting formulation was applied in four equal cross coats having a total thickness of 4.5 - 6.5 mils one-half hour between coats (4 hours dry). Over this was applied two coats MIL-C-81773 aliphatic polyurethane (1 hour dry) having a total thickness of 1.0 - 1.5 mils. The assembly was allowed to air cure for one week.

Example 2

54.5 parts by weight of a fully saturated urethane prepolymer which is known as Adiprene L-42 (DuPont) was ground in a closed pebble mill with 34.0 parts by weight of toluene which had been dried over sodium. Two volumes of the resulting suspension were then mixed with one volume of a curing agent which consisted of 4.8 parts by weight of 4,4' ethylene-bis-2-chloroaniline
and 34.6 parts by weight of methyl ethyl ketone (urethane grade). The resulting formulation was then applied in the same manner as Example 1.

Example 2

54.5 parts by weight of a fully saturated urethane prepolymer which is known as Adiprene L-100 (DuPont) was ground in a closed pebble mill with 34.0 parts by weight of toluene which had been dried over sodium. Two volumes of the resulting suspension were then mixed with one volume of a curing agent which consisted of 6.63 parts by weight of 4,4'-methylene-bis-2-chloroaniline and 33 parts by weight of methyl ethyl ketone (urethane grade). The resulting formulation was then applied in the same manner as Example 1.

Six of the aluminum alloy fatigue assemblies were coated as described for each of the resulting formulations of Examples 1, 2 and 3. Two assemblies of each formulation were allowed to air cure, one for four hours and one for twenty hours. Two assemblies were air dried one week and baked for 20 hours at 260° F plus one hour at 325° F. This baking is equivalent to one PAR (progressive aircraft rework) heating. The remaining two assemblies were air dried one week and baked for forty hours at 260° F plus two hours at 325° F (2 PAR heating). Each assembly was then loaded in a Krous fatigue machine to 1,000 - 11,000 lbs. and fatigued for 1,000 cycles at -60° F. The -60° F temperature was used as being typical of that encountered during flight.

The assemblies coated as described in Example 1 did not crack around any fastener heads during the cyclic loading, either non-baked or baked to approximate a one PAR heating. After the two PAR simulated heat cycle, the coatings cracked
around approximately 70% of the fastener heads. No blistering occurred. Less stress marks were noted around the fastener heads with the formulation of Example 1 than with the formulations of Examples 2 and 3.

The assemblies coated as described in Example 2 did not crack around any fastener heads during the cyclic loading either non-baked or baked to approximate a 1 PAR heating. After the two PAR simulated heat cycle, the coating cracked around approximately 50% of the fastener heads during the cyclic loading. Some stressing around the fastener heads was also noted. No blistering occurred.

The assemblies coated as described in Example 3 were then tested. The unbaked assemblies did not crack around any fastener heads during the cyclic loading. The assemblies that were baked to approximate the one and the two PAR heat cycles had cracking around all fastener heads during the cyclic loading. Blistering occurred on only the panel with the four hour air cure.

No delamination occurred at any interface with any of the coatings evaluated. It has been calculated that 1,000 cycles of the 11,000 lb. upper limit cyclic loading on the specimens used for these tests approximate the spectrum of stresses which would occur on high performance military aircraft during 500 flight hours (approximately 1 PAR cycle or 15 months). A 1700 lb. stress represents minimum stress to which an aircraft is subjected in steady state flying conditions without acceleration or deceleration. The 11,000 lb. high stress level corresponds to an approximate 7G maneuver.

From the tests, it appears that either the formulation of Example 1 or Example 2 will protect the fastener head area.
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from cracking after at least a one hr simulated heat cycle.
The formulation of Example 1 is considered somewhat better, however, in that less stress marks appear in the topcoat at the fastener edge during the cyclic loading.

It has therefore been described a method for protecting the aircraft skin fastener head areas by means of a sealant when frictional heating up to 325°F for short periods of time occur at the head areas.

It will be understood that various changes in the details, materials, steps and arrangements of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art.