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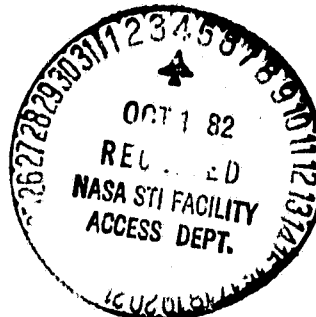
(NASA-Case-ARC-14408-1) HIGH PERFORMANCE CHANNEL INJECTION SEALANT INVENTION ABSTRACT Patent Application (NASA) 21 F HC A02/HF A01

N82-33523

CSCI 11A

G3/27

Unclass 27538



ARC

THIS NASA INVENTION APPEARS TO HAVE EXCELLENT COMMERCIAL POTENTIAL

AUG 20 1982

SERIAL NO. 403,371

FILE DATE: JULY 30, 1982

NASA Case No. ARC-11408

High Performance Channel Injection Sealant

Invention Abstract

A channel sealant having high performance characteristics is disclosed. The sealant is based on NASA-patented cyano- and diamidoximine-terminated perfluoroalkylene ether prepolymers that are thermally condensed and cross-linked. The sealant contains asbestos and, in its preferred embodiments, Lithofrax to lower its thermal expansion coefficient and a phenolic metal deactivator.

The sealant was extensively evaluated by Hughes Aircraft Company under Contract NAS-2-10334. In this evaluation it was shown to be extremely resistant to thermal degradation with an onset point of 280°C. The materials had a volatile content of 0.18%, excellent flexibility and adherence properties and fuel resistance. No corrosibility to aluminum or titanium was observed.

The present materials are easily processed and can replace existing channel sealants.

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Hughes Aircraft Company

SN- 403-371
File Date July 30, 1982

HIGH PERFORMANCE CHANNEL
INJECTION SEALANT

Origin of the Invention

5 The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

10

Technical Field

Satisfactory sealing of irregularly-shaped riveted bolted and spot-welded wing and fuselage cavities for use as fuel tanks has been a problem since these assemblies were first proposed for aircraft use. It is known to use filled elastomeric materials for sealing such cavities. These materials are referred to as channel sealants and are ideally characterized by resistance to deterioration by fuel, good adhesion to metals, permanent flexibility and resistance to vibrational, thermal and mechanical stresses. Classic channel sealants usually maintained these desired properties at temperatures ranging from -54°C to +71°C. With the advent of higher speed and supersonic aircraft, the temperature requirements have increased from 71°C to as high as 177°C (and 315°C projected) with a corresponding increase in the stresses placed on the sealant materials.

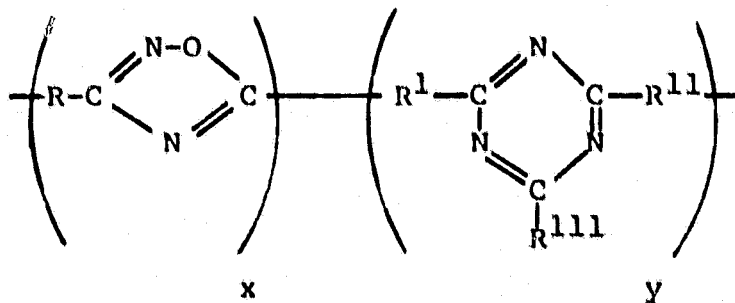
The increased stresses to which the sealants are subjected in the faster flying, hotter aircraft are both physical and chemical in nature. For example, at the higher temperatures, the sealants expand more, thus placing higher adhesive and cohesive stresses on the sealants and the sealant-to-metal bonds. The tendency for depolymerization or, conversely, additional cross-linking (stiffening) is increased, which in either case could lead to sealant failure. The rate of chemical reaction, either with fuel, fuel additives or with absorbed water, is considerably increased. Even the vibration rates and the "g" forces are

increased, leading to mechanical adhesive or cohesive failures.

The present invention provides new channel sealants which can stand up to these stresses. They employ as their base polymers, fluoropolymers - particularly triazine-crosslinked, 1,2,4-oxadiazole elastomeric fluoropolymers. Polymers of this general type and related non-crosslinked materials are disclosed in United States Patent 4,145,524 of Ross and Rosser (issued March 20, 1979) and United States Patent 4,285,085 of Rosser, Shalhoub and Kwong (issued January 13, 1981). Their preparation is claimed in United States Patent 4,273,918 issued to Rosser et al on June 16, 1981. Although these patents suggest the use of their polymers in seals, sealants and gaskets, they do not suggest the particularly advantageous, particularly high performance materials of this invention.

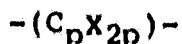
Statement of the Invention

It has now been discovered that when formulating a filled fluoropolymer channel sealant based on triazine-crosslinked 1,2,4-oxadiazole elastomeric fluoropolymers, superior properties are achieved when the filler comprises asbestos and the ratio of 1,2,4-oxadiazole groups to triazine groups is controlled to within certain limits. Thus, this invention provides filled fluoropolymer channel sealants comprising asbestos fibers dispersed in a triazine ring-crosslinked 1,2,4-oxadiazole elastomeric polymer of the formula

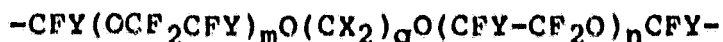


wherein R, R¹, R¹¹ and R¹¹¹ are each bivalent radicals and

independently selected from alkylene radicals of the formula



and alkylether radicals of the formula



5 In these formulae, X is fluorine or hydrogen, Y is fluorine or trifluoromethyl, p is a number from 2 to 18 inclusive, q is a number from 1 to 18 inclusive, and m+n is from 2 to about 9 inclusive. In these formulae the ratio of x:y is from about 6:1 to 1.25:1.

10 These sealants can contain other materials, with metal deactivators and thermal expansion stabilizers offering particular advantages.

The polymers employed in these sealants may alternatively be defined as products of the thermal condensation of
15 certain amidoxime and diamidoxime fluoromonomers with certain triazine ring-forming nitrile or amidine fluoromonomers.

Detailed Description of the Invention

The sealant compositions contain asbestos and fluo-
20 ropolymer and optionally a metal deactivator and a thermal expansion stabilizer.

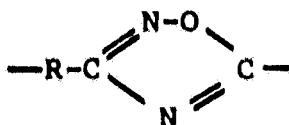
Asbestos

The asbestos component is employed for thixotropy
25 and reinforcement. The asbestos is employed as fibers. The amounts employed and preferred are given below in the "Formulations" section. Asbestos provides an unexpectedly advantageous product. Certainly, the safety concerns about asbestos would suggest alternative materials such as glass
30 fiber, aramid fiber or processed mineral fibers. These materials do not give equivalent products - either refusing to mill into the polymer at required substantial loadings or not giving a uniform product. Commercial asbestos is fully satisfactory with such products as Union Carbide's RG-244 "Calidria"
35 being exemplary.

The Polymer

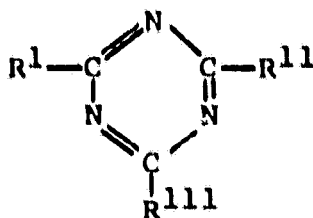
The polymer used in these sealants is a fluoropolymer containing 1,2,4-oxadiazole linkages

5



and triazine linkages

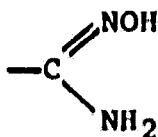
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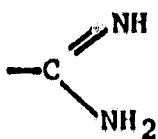
15 The relative amounts of these two linkages must be controlled. Based on amounts of reactants fed to theoretically generate these two ring structures, there should be at least 1.25 oxadiazole rings for each triazine ring. Suitably the ratio of these linkages is in the range of 1.25:1 to 6:1. Preferably this ratio is from 1.5:1 to 4:1. More preferably it is from 1.75:1 to 2.25:1 with best results being observed when the ratio is about 2:1.

25 The placement of these linkages relative to one another on a gross molecular basis is random. The relation of these linkages to one another on a "micro" basis may be somewhat more controlled and will depend upon the monomers employed to prepare the polymer. For example, some bifunctional monomers can only form triazine rings. Thus if both ends of such a monomer react, two triazine rings will be adjacent. With bifunctional monomers that can form either type of ring at either end, a fully random pattern would be expected.

35 These polymers are prepared by the heat-induced condensation of one or more bifunctional monomers that together contain amidoxime groups

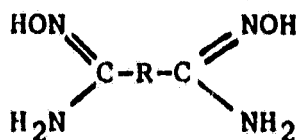


5 and nitrile groups $\text{-C} \equiv \text{N}$ and/or amidine groups



10 These monomers may include:

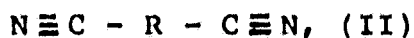
diamidoximes of formula I



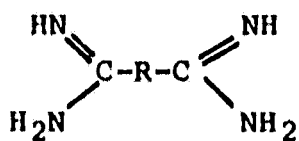
(I)

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dinitriles of formula II



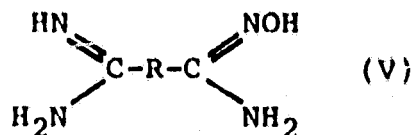
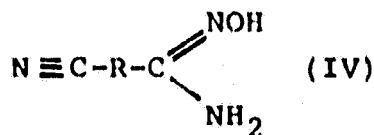
diamidines of formula III



(III)

20

and amidoxime hybrids of the formulae IV and V



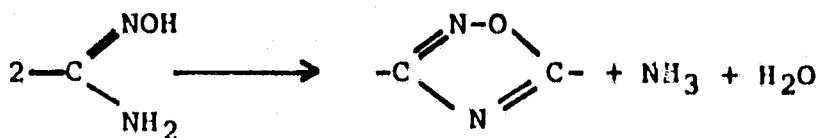
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wherein R is a bivalent organic radical.

These materials can enter into a variety of reactions when heated together, including:

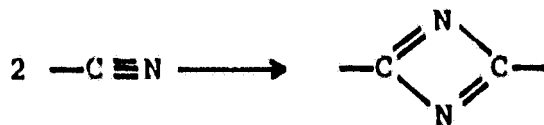
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Two amidoximes can form a 1,2,4-oxadiazole

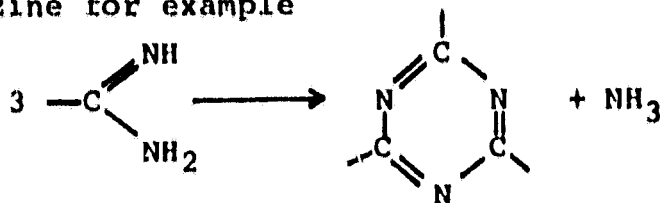


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Two nitriles and/or amidines can form a four membered ring, for example

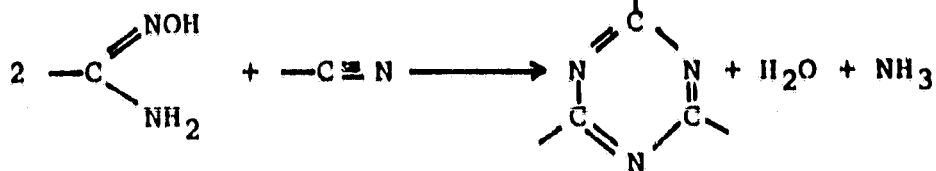


5 Combinations of three nitriles and/or amidines can form a triazine for example



10

In addition one or two amidoximes can react with two or one nitrile or amidines to give a triazine, for example



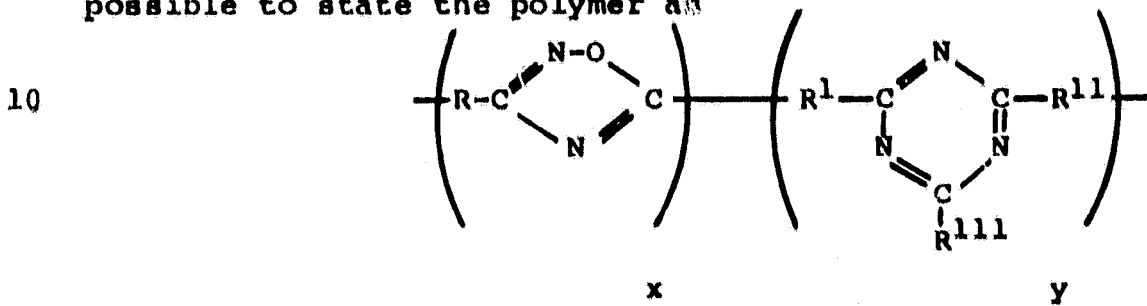
15

20 Analysis of the polymer products shows the presence of triazine and oxadiazole linking groups. The elastomeric nature of the product shows that the triazines serve as cross-links between the chains.

25 The polymers employed in these sealants may be defined as the triazine and oxadiazole group-containing polymer resulting from the thermal condensation of certain specified ratios of feedstocks. That is, they are the thermal condensation polymers of the aforesaid diamidoximes, dinitriles, diamidines and amidoxime hybrid monomers and admixtures thereof, said monomers being selected to provide from
30 6.5 to 1.5 times as many amidoxime groups as nitrile groups plus amidine groups. At ratios outside this range, the most advantageous channel seal properties are not obtained. Preferably the ratio of amidoxime:nitrile plus amidine is from 4.5:1 to 2:1, more preferably from 3:1 to 2.25:1 and most
35 preferably about 2.5:1.

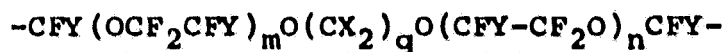
While, as is normal in polymer chemistry, it is not possible to readily determine the precise proportion of groups

in the complicated multigroup crosslinked product which is itself a statistical average of a variety of products, it is possible to assign a formula to the polymers employed. This is done by assuming that all the amidoxime, amidine and nitrile groups fed react to form 1,2,4-oxadiazoles and triazines and that the triazines are each formed from two nitriles or amidines and one amidoxime. With these assumptions, it is possible to state the polymer as



wherein R, R¹, R¹¹ and R¹¹¹ are each bivalent organic radicals and the ratio x:y ranges from 6:1 to 1.25:1, preferably 4:1 to 1.5:1, more preferably 2.25:1 to 1.75:1 and most preferably about 2:1.

20 In these polymers each of the R's is a bivalent organic radical. Each R is selected independently. These radicals include preferably linear but also branched alkylene and perfluoroalkylene radicals of the formula -C_pX_{2p}- wherein p is a number from 2 to 18, preferably 5 to 12, and X is hydrogen or preferably fluorene. These R's also include bivalent oligomeric oxyfluorocarbon radicals of the formula

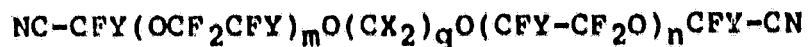


wherein Y is F or CF₃, q is a number from 1 to 18 and m and n are each numbers from 1 to 5 inclusive the sum of which is from 2 to 9. In these perfluoroalkylethers, preferably q is a number from 2 to 12, more preferably 3 to 7 and especially 5. Preferably m and n are equal and are each 2 or 3.

Feedstock Preparation

35 The diamidoxide, diamidine and hybrid feedstocks can all be prepared from the corresponding dinitriles.

The dinitriles, NC-(R_f)-CN, include preferably linear but also branched fluorocarbon dinitriles, NC-C_pF_{2p}-CN. These materials are known and may be prepared from the corresponding diacids which are marketed commercially by PCR Research Chemicals, Inc. This preparation involves successively converting the diacid to a diacylfluoride to a diamide and finally to the dinitrile. This process is shown in detail in United States Patent 4,145,524. The NC-(R)-CN dinitrile may also be selected from oligomeric (perfluoroalkylether) dinitriles,

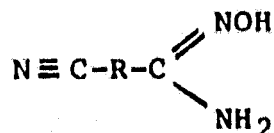


wherein Y, m, q and n are as already defined. These materials are known and can be prepared as taught in U.S. Patent 3,347,901 of Fritz, et al. Many of these materials are also available from PCR, Inc. R represents the bivalent perfluorinated radicals which correspond to these dinitriles. Mixtures of two or more dinitriles may be used, as well.

The diamidoximes can be formed from these dinitriles by the method shown in United States Patent 4,145,524 wherein the nitriles are reacted with hydroxylamine or especially a hydroxylamine salt.

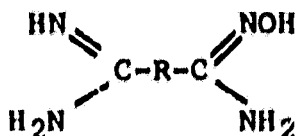
The diamidine feedstocks can be prepared by the method disclosed in United States Patent Application _____ (NASA case ARC - 11402), wherein the corresponding dinitrile is reacted with a large excess (10-200 molar excess) of ammonia at low temperatures such as -60°C to -33°C to yield the diamidine.

The hybrid feedstock



can be prepared by the method shown in United States Patent 4,273,918 wherein the corresponding dinitrile is reacted with limited amounts of hydroxylamine with or without an absolute alkanol solvent. The product can be worked up to give a pure hybrid or may be used as a mixture.

The hybrid feedstock



5

can be prepared by the method also shown in United States Patent 4,273,918 wherein the corresponding dinitrile is reacted with limited amounts of hydroxylamine and thereafter reacted with ammonia.

10 The disclosures of these preparations in these referenced patents and patent application are incorporated herein by reference. It should also be understood that other equivalent preparation methods can also be used.

15 The Polymer Forming Reaction

The polymer is formed by thermally condensing the appropriate mixture of monomers. This condensation is effected at a temperature within the range of 50°C to 300°C, preferably from 100°C to 250°C. The cure time is a function of the temperature employed and ranges from 5 to 250 hours or longer, if desired. Although not required, a staged temperature cure can be used. For example

- 3-10 hours at 100-140°C,
- 40-150 hours at 140-165°C, and finally
- 25 15-75 hours at 165-195°C.

In general terms, the product of full cure is a high molecular weight cross-linked material. The intermediate products, such as the product after say 50 hours at 155°C cure would have a less cross-linked structure and a molecular weight of 5000-35000, typically.

A vacuum may be employed especially during the final stages of curing. Use of vacuum should be carefully watched as it has the effect of pulling off volatile products and may vary the nature of the final product. As evidenced by these high cure temperatures, it is a great advantage of these polymers that they can withstand temperatures as high as 300°C and even 350°C in some cases without degradation and generally

exhibit weight losses of less than 5% during 15 hours at 300°C.

Optional Ingredients

5 The channel sealants of the invention may advantageously contain other ingredients. These include metal deactivators, thermal expansion coefficient stabilizers, colorants, pigments and the like.

10 The metal deactivators are added to improve the aging properties of the sealant especially when it is in contact with metals. These materials minimize loss of tack and loss of adhesion to metals and maintain the sealant's flexibility with age. Metal deactivators are known to the art and can include alkylated oxyaromatics including alkylated
15 phenols and bis-phenols, alkylidene bis-, tris- and polyphenols and alkylated hydroquinones such as hindered alkyl phenols and hydroquinones, for example, ditertiary butyl phenol, tertiary butyl hydroquinone, ditertiary butyl p-cresol and the like.

20 The thermal expansion coefficient stabilizers that can be added are inert inorganic powder fillers selected to lower the thermal expansion coefficient of the sealant. Their incorporation allows the sealant to be used at even wider temperature extremes. The metal aluminum silicates - e.g., lith-
25 ium aluminum silicate, calcium aluminum silicate and the like are suitable with lithium aluminum silicate being preferred.

 Colorants, pigments and the like may also be added if desired as may minor amounts of other materials without departing from the spirit of this invention.

30

Formulations

 Channel sealant formulations of this invention comprise the following materials on a weight basis

35	Polymer	1 part
	Asbestos	0.05 - 0.5 parts
	Metal Deactivator	0 - 0.2 parts
	Thermal Expansion Stabilizer	0 - 1 parts

Preferred sealants contain

	Polymer	1 part
	Asbestos	0.075 - 0.3 parts
	Metal Deactivator	0.01 - 0.1 parts
5	Thermal Expansion Stabilizer	0.3 - 0.8 parts

More preferred sealants contain

	Polymer	1 part
	Asbestos	0.1 - 0.2 parts
10	Metal Deactivator	0.01 - 0.10 parts
	Thermal Expansion Stabilizer	0.45 - 0.65 parts

Most preferred sealants consist essentially of

	Polymer	1 part
15	Asbestos	0.15 parts
	Metal Deactivator	0.05 parts
	Thermal Expansion Stabilizer	0.55 parts

Preparation

20 The sealants can be simply prepared by admixing the asbestos and the optional ingredients into the polymer before but preferably after the polymer has fully or partially cured. This may be accomplished by conventional mixing, milling or the like. This is purely a physical mixing and it
25 is carried out as needed to give a uniform product.

 The sealants of this invention, their preparation and their advanced properties will be shown by the following examples. These are provided to describe the invention and are not intended to limit its scope.

30

Examples

 In these examples, all temperatures are in °C, and all weights are in g unless otherwise noted. Infrared (IR) spectra were recorded on a Nicolet MX-1, FT-IR Spectrometer.
35 Thermogravimetry measurements were recorded with DuPont Instruments, the 951 thermogravimetry analyzer and the 990 thermal analyzer.

Feedstock Preparation

Example I

The dinitrile $N \equiv C-R-C \equiv N$, wherein R is $-\text{CF}(\text{CF}_3)-(\text{OCF}_2\text{CF}(\text{CF}_3))_m-\text{O}-(\text{CF}_2)_5-\text{O}-(\text{CF}(\text{CF}_3)-\text{CF}_2-\text{O})_n-\text{CF}(\text{CF}_3)-$
5 was obtained from PCR Research Chemicals, Incorporated. The sum of $m+n$ was, on average, 6 with 95% of the material having this value. 5% had higher and lower values, e.g. 5 or 7.

Example II

10 The corresponding diamidoxime was prepared. In a representative small scale preparation, 0.23 g (0.01 mol) of sodium was reacted with 20 ml of methanol. The solution was cooled and 0.70 g (0.011 mol) of hydroxylamine hydrochloride was added. The mixture was stirred for 1 hour as sodium
15 chloride precipitated. The sodium chloride was filtered and to the solution was added 5 g (0.004 mol) of the Example I dinitrile in 20 ml of Freon 113. The reaction was stirred overnight and the solvent was removed in vacuo, leaving 5 g
20 (99%) of a gummy residue. The product was dissolved in Freon 113, filtered and concentrated to dryness leaving 4.8 g (96%) of the diamidoximine.

Analytical data: IR (film): 2.85 (OH), 5.85, 5.90, 6.26 (C=N), 7-9 (CF).

25 Example III

Preparation of the corresponding diamidine was accomplished in the following representative manner. Twenty milliliters of NH_3 were condensed into a 100-ml, three-neck flask equipped with a dry-ice condenser, an NH_3 gas inlet, and
30 an addition funnel. A solution of 10 g of the dinitrile of Example I in 10 ml of Freon 113 was added dropwise into the flask with vigorous stirring.

After completion of the addition, excess ammonia and Freon 113 were removed by vacuum. Liquid perfluoroalkylether
35 diamidine (105 g) substantially free of ammonia was then collected without further purification.

Analytical data (IR liquid film): 3200-3000 cm^{-1} (NH); 1684 cm^{-1} (C = N); 1400-1050 cm^{-1} (C - F).

Example IV

5 In a representative reaction an amidoxime-nitrile hybrid was prepared by placing 0.355 g of hydroxylamine in a round-bottomed flask and adding 9.0154 g of the dinitrile of Example I with 20 ml of Freon 113. The flask was purged with nitrogen gas and the contents stirred overnight. The solution
10 was removed from the flask and the solvent evaporated with nitrogen gas to give 8.07 g of the amidoxime-nitrile, in 85% yield. Infrared analysis of the product showed absorption at 2.86 μm ; 2.96 μm (NH_2); 2.98 to 3.32 μm (OH); 4.43 μm ($\text{C}\equiv\text{N}$); 5.96 μm (C = N); 6.33 μm (C = N); and 7 to 9 μm (C - F). The
15 ratio of nitrile to amidoxime was 1:10.8.

Example V

An amidoxime-amidine hybrid was prepared in a representative reaction by stirring together in a nitrogen
20 atmosphere for 16 hours 11.02 g (7.2 mmoles, 1.14 molar equivalents) of the dinitrile of Example 1, with 0.28 g (8.48 mmoles) hydroxylamine diluted with 30 ml Freon 113. Ammonia was then bubbled into the solution for 1 hour at room temperature. This gave 10.55 g (93.5% yield) of the hybrid
25 having a 1:1.43 ratio of amidine to amidoxime groups, IR absorption was measured at 2.84 to 3.02 μm (NH_2); 2.97 to 3.32 μm (OH); 5.77, 5.95, and 6.33 μm (C = N amidoxime); 6.06, 6.25 μm (C = N) amidine); and 7 to 9 μm (CF).

30 Examples VI-XV

Examples I-V are repeated varying the starting nitrile such that in Examples VI-X $\text{R} = (\text{CF}_2)_8$ and in Examples XI-XV $\text{R} =$ a perfluoroether wherein $n+m = 4$ and $q = 7$. Equivalent products are obtained.

Polymer Preparation and Sealant Formulation

Example XVI

Ten grams of the diamidoxime of Example II and four grams of the dinitrile of Example I were intimately mixed and poured 1/4" deep into a flat container which was placed in a convection oven and heated. Periodically the mixture was stirred. The heating schedule was 127°C - 6 hours, 154°C - 70 hours and finally 177°C - 24 hours. This produced an elastomeric polymer useful as a sealant base.

10 An optimum sealant (XVI) was formulated from the polymer. It contained

Polymer	10.0 parts by weight
Asbestos	1.5 parts by weight
Lithium Aluminum Silicate	5.5 parts by weight
15 Metal Deactivator, Irganox MD-1024	0.5 parts by weight

First, the asbestos was milled in to achieve proper wetting of the fibers, which took at least 30 minutes on a rubber micromill. Then, the other fillers were added gradually and milled until the polymer banded correctly on the mill. The entire milling process was performed in a dry box especially set up for working with asbestos. The rubber mill was manufactured by Coastcraft Rubber Co., Inc. It is a two roll mill; the roll diameters are 1 inch and 1.175 inches. The roll speed is 19 rpm. It has a 1/3 horsepower motor.

25 The polymer was removed from the rollers after compounding and post-cured another hour at 154°C before test samples were prepared.

Because of the safety problems inherent in the use of asbestos, two alternate reinforcing fibers, processed mineral (PMF) and aramid (Kevlar), were investigated. The PFM filler at a 35 percent loading could not provide the strength necessary as evidenced by excessive flow at higher temperatures. The extensive milling that was required chopped up the fibers and reduced their strength. Kevlar fibers of 0.16 cm (0.062 inch) length were difficult to mill in, and only a 5 percent loading was achieved. Furthermore, the product was stringy and not uniform. These comparative formulations are shown in the table in Example XVII.

Example XVII

The preparation of Example XVI was repeated with various modifications to the formulation, including the above-noted tests with Kevlar and processed mineral. These formulations are shown in the following table.

CHANNEL SEALANT FORMULATIONS

Sealant	Polymer	Lithafrax LiAl Silicate	Asbestos	MD-1024	Other
	XVIIa	5.0 parts	5.0 parts	0.25	0
10	b	5.0	2.75	0.75	0.24
	c	5.0	2.65	0	0.25
	d	5.0	2.75	0.70	0.20
	e	5.0	2.75	0.75	0
	f	5.0	2.75	0.60	0.25
15	g	5.0	2.75	0.75	0.25
	-	5.0	2.75	0	0.25 (Kevlar)
	-	5.0	2.75	0	0.25 (PMF)

Example XVIII

The preparation and formulation of Example XVI is repeated varying the polymer as follows:

Example	Polymer Composition	
	Material of Example,	Parts by Weight
XVIII	III - 2 parts	II - 10 parts
XIX	III - 4 parts	II - 10 parts
25 XX	IV - 8 parts	II - 6 parts
XXI	V - 8 parts	II - 6 parts
XXII	I - 4 parts	VII - 10 parts
XXIII	XI - 4 parts	II - 10 parts

The sealants of Examples XVI and XVII were tested to determine their suitability and properties. They were seen to have a volatile s content of about 0.1%, far below the maximum allowable of 2% (MIL-S-81323 (WP)). The materials' potential and performance as sealants were then evaluated. The materials were subjected to pressure rupture resistance, and peel adhesion testing after fuel immersion and heat aging. Low temperature flexibility was also evaluated.

Pressure rupture resistance was evaluated per the procedure outlined in MIL-S-81323. The sealing compound was packed into three blowout specimens and stabilized at 25°C for 24 hours. The specimens were cooled to below -29°C. The specimens were then tested as described below. One specimen was mounted in the pressure rupture jig. One air hose bib of the apparatus was connected to a manometer, the other to a variable pressure source. The assembly was immersed in a water bath at 25°C and stabilized for 5 minutes. Starting at atmospheric pressure, the pressure was increased uniformly at the rate of 1 inch of mercury per 15 seconds until failure occurred. A continuous stream of air bubbles coming from the specimen constituted failure. Three specimens were tested as above. Three other samples were immersed in JRF for 120 hours at 49°C plus 6 hours at 71°C and 6 hours at 82°C. These were then removed and tested as described above for pressure rupture resistance. Another set of three samples were tested for pressure rupture resistance at an elevated temperature by placing the pressure rupture jig assembly in an oven at 177°C and testing after stabilization for 15 minutes. Failure was indicated by a rapid drop in pressure.

Pressure rupture testing was evaluated on formulation XVIIc originally rejected because of a lack of tack and adhesion. The use of a 1-hour test aging step at 177°C after milling made the formula tacky. This formulation was evaluated for resistance to pressure rupture. The results demonstrated that the sealants far exceed the minimum requirements per MIL-S-81323 (WP) both before and after exposure by as much as eightfold.

Adhesion in peel was evaluated on the formulation of Example XVI per MIL-S-81323. Test samples were prepared between aluminum plates. After conditioning the prepared plates for 24 hours at 77°F and 50 percent relative humidity the plates were peeled apart at a slow steady rate.

The results showed a 100 percent cohesive failure exceeding the 95 percent cohesive failure requirement.

A low temperature flexibility test was performed as described below. The sealant was applied as a 10.2 x 0.64 centimeters strip on a 15.2 x 2.54 x 0.16 centimeters aluminum coupon. The test fixture consisted of a support fixture with a 10.2 cm span and a circular mandrel 10.2 cm in diameter. The sample and test fixture were placed into an environmental chamber mounted on an Instron Mechanical Testing machine. The environmental chamber was then cooled to and maintained at -54°C. After thermal equilibrium, the sample was placed on the support fixture and the mandrel placed on the sample. After another period of thermal equilibration, the mandrel was driven down 3.94 cm at a rate of 50.8 cm/min, bending the sample around the mandrel. The load was removed, then the sample was examined for cracking, flaking and other failures. Formulation XVI tested in this manner developed four cracks 0.16 cm in length at the outside edges of the sample which were deemed insignificant. The material did not flake and otherwise kept its integrity.

Gap sealing efficiency testing on formulation XVI was initiated per MIL-S-81323 (WP) using 5 mil spacers. The sealant was pressed by hand into the groove of a jig, which was then closed up, tightened and leak tested at 10 psi. The jig, containing 3 percent aqueous sodium chloride, was then immersed in a water bath, heated to 49°C.

The testing schedule for cap seal efficiency was 49°C for 25 days, then 71°C for 60 hours, then 82°C for 6 hours.

The jig was drained, placed in an oven at 177°C, stabilized and checked for leakage at 5 psi for 2 hours. Then

a pressure of 10 psi was applied for one minute, and the jig was checked for leakage. A second jig was set up similarly containing jet reference fuel (JRF) and also immersed in a 49°C water bath.

- 5 The test schedule for the second jig was
 49°C for 100 hours, then
 71°C for 10 hours, then
 82°C for 1 hour.

The jig was drained and dried in an oven at 107°C for 20
10 hours, 10 hours at 154°C and 1 hour at 177°C with 5 psi applied continuously. Then the pressure was increased to 10 psi for 1 minute.

The gap sealing efficiency test of the material was repeated with 10 mil spacers using the test schedule of the
15 jig filled with JRF. These results indicate that the material was able to satisfactorily seal 5 and 10 mil gaps.

Fuel resistance was determined per MIL-S-81323 (WP) for formulations XVI and XVII g. After 25 days immersion in JRF at 49°C, samples of XVI showed an average of 12.44 percent
20 volume change (swelling). Samples of XVII g were immersed in JRF for 25 days at 49°C, plus 60 hours at 71°C, plus 6 hours at 82°C. The volume change and weight change for these samples averaged -9.93 percent and -0.24 percent, respectively. A separate sample of XVI had a volume change of -6.87
25 percent in this test. These results were far superior to conventional materials.

The materials were evaluated for thermal stability by TGA. These tests showed that the temperature for onset of degradation was outstandingly high, running as high as
30 330-360°C for the polymers and 270-300°C for the sealants.

HIGH PERFORMANCE CHANNEL
INJECTION SEALANT

Abstract

Channel sealants suitable for high stress applica-
5 tions such as sealants for fuel tanks in high performance
aircraft are disclosed. The sealants include asbestos dis-
persed in triazine-crosslinked 1,2,4,-oxidiazole polymers.
Optionally, the sealants include a metal deactivator and/or a
thermal expansion coefficient stabilizer.