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# POLYMER SYSTEMS FOR RAPID SEALING OF AIRCRAFT STRUCTURES AT LOW TEMPERATURE

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)  Materials examined for low temperature, rapid curing, fuel and water resistant sealants included hot melts, UV activated, moisture curing, and anaerobic polymers. Two component polymers utilizing urethane cures, oxidation, and mercaptan-epoxy additions were evaluated: Epoxy cures of mercaptan terminated polythioethers gave excellent low temperature cures along with practical application times. Physical and chemical properties were examined and found to essentially meet requirements of MIL-S-85420 (AS). Storage stability was excellent.						
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FORWARD

This Final Report describes work by Products Research and Chemical Corporation during the period September, 1981 to August, 1983 on Contract Number N62269-81-C-0741, "Polymer Systems for Rapid Sealing of Aircraft Structures at Low Temperature" by the Naval Air Development Center (NADC), Warminster, Pennsylvania. Coleman Nadler was the NADC technical monitor.

The program manager at Products Research was Lester Morris. Laboratory research was conducted by Dr. Morris Williams and Nicholas Champlin.



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## I. INTRODUCTION

Field repair of military aircraft frequently must take place under very adverse conditions. There is little or no control of the temperature. Time available before turn around of the aircraft may be quite limited.

Structural repairs, sealing electrical equipment against water entrance, patches, leaks, windshield installations, etc. utilize sealants as part of the repair process.

The standard aircraft sealants are traditionally based upon polysulfides because of their general overall resistance to fuel, water, weather, and low temperature. Two fast curing polysulfide materials which were studied for the development of low temperature cure sealant specification MIL-S-85420 (AS) utilize a dichromate cure and a manganese dioxide conversion. It has been found, at NADC, that the rapid curing version of the manganese dioxide cured material, on aging, fails to cure rapidly enough at 45°F. On the other hand, the dichromate based material, while age stable, requires 8 hours or more at 45°F before conversion to a suitable thermoset condition occurs. Further, the fastest materials have been so speeded up to meet the low temperature conversion rate, that their mixing and available application time at ambient temperatures is limited to a relatively short period, approximately 8 to 10 minutes.

It was the object of this program to find sealant materials and or methods which would allow rapid turn around times of aircraft at low temperatures, provide age-stable products, and yield practical working or application times. It was further expected that the materials would essentially meet or exceed the performance requirements of MIL-S-8540 (AS) and give properties similar to MIL-S-8802 materials.

A number of potentially useful chemical and physical methods of improving the relationship between cure at low temperatures and ambient application life have been suggested:

- A. Hot melt materials "set" on cooling and are therefore nearly independent of temperature for their hardening action.
- B. Materials which show activation by free radical mechanisms are much less dependent on temperature for conversions than are usual two

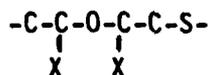
component systems. Ultra-violet induced free radical conversions are especially rapid. Anaerobic cures are also free radical initiated and are candidates.

- C. Catalyst application to a relatively slow converting product can combine good application life with rapid cure.
- D. Two component systems with low heats of activation or long induction periods might also show flat temperature responses.

All of the foregoing approaches were examined with the greatest amount of time devoted to perfecting two component systems.

Polysulfide liquid polymers, traditionally have been the standard of the industry. PRC manufactures high sulfur liquid polymers trade named Permapol® P-3, which are fuel and water resistant. These polymers can be chemically modified at their terminals to offer raw materials which can be relied upon for basic environmental resistance and yet can be varied chemically to explore the effects of various curing mechanisms on the cure rate at various temperatures. Many of the derivatives cited in the program were, therefore, conveniently prepared from the polythioether backbone.

Permapol® P-3 is manufactured under U.S. Patent No. 4,366,307. The basic polymer consists of the following structure:



Terminals which are available during regular commercial manufacturing include OH, C=C, and SH. In the above structure, X is methyl or hydrogen with the methyl to hydrogen ratio varying, but typically being about 30 mole percent.

## II. SUMMARY

The initial portion of the experimental effort involved determining the relative chemical curing rates of two component systems at 77°F and 40°F. These rates were compared with the cure rates of the best dichromate and manganese dioxide cured Thiokol polysulfides studied during development of MIL-S-85420 (AS), Sealing Compounds, Quick Repair Low Temperature Curing Polysulfides for Aircraft Structures.

Emphasis was on developing stable, rapid curing, easy handling oxidation cures of PRC mercaptan terminated polythioethers. Other major two component efforts involved isocyanate terminated polythioethers with amines, and mercaptans with epoxy resins.

Single component compositions examined for suitability as quick repair materials included polyethylene acrylate hot melt (Vamac), zinc salt ionomer of a mercaptan terminated polythioether, UV activated acrylic terminated polythioethers, moisture cures of alkoxy silane terminated polythioethers, and an anaerobic material. All of the single component systems had disadvantages for general quick repair applications.

The two component materials based upon oxidation cures of mercaptan terminated polythioether (Permapol P-3 with 28% sulfur) and the reaction of this mercaptan with epoxy resins offered the most promise. These were further examined for physical properties before and after environmental exposures.

The epoxy-mercaptan reaction was clearly superior from the stand point of low temperature cure rate versus application time at room temperature. Numerous formula variations were prepared and properties examined. Storage stability was found to be excellent and optimized formulations showed general conformance to the application and performance requirements of target specification MIL-S-85420 (AS). Samples of several variations have been submitted to the Naval Laboratories in Warminster, Pennsylvania, along with appropriate primer.

### III. DESCRIPTION OF INITIAL SCREENING WORK

#### A. Exploration of Two Component Systems

##### 1. State of the Art

In evaluating the potential of a two component material, the ratio of the cure rate at 40°F to that at 77°F was an initial determination. As a goal for an acceptable two component product, it was deemed desirable that the material achieve a Rex hardness of 20 in 4 hours at the low temperature and/or [a minimum of 20 psi in the blow out test per MIL-S-85420 (AS)] and at least a 15 minute working time at room temperature.

The relative cures of two products being considered for quick repair materials is shown:

TABLE I

Comparing Initial and Aged Cure Hardening of MIL-S-85420 Candidates  
Dichromate Cured - 1/4 hr. and Manganese Cured - 1/4 hr.  
at 77°F and 40°F

	Dichromate Accelerated Material		Manganese Dioxide Material	
	<u>Initial</u>	<u>Aged 6 mos. RT</u>	<u>Initial</u>	<u>Aged 6 mos. RT</u>
Appl. Life, 77°F minutes	15	12	15	12
Hardness, 24 hrs. Shore A	50	55	40	35
Hardness, 40°F Shore A				
@ 4 hrs.	1	2	6	no cure
@ 8 hrs.	8	12	15	no cure

After 6 months aging at room temperature the manganese dioxide cured material failed to cure at 40°F while the dichromate based material is essentially unchanged or has improved somewhat in cure characteristics. The 8 hours time to thermoset of dichromate based material definitely extends the turnaround time of repaired aircraft. A major objective of this program was to reduce such time to 4 hours with a product that would desirably meet the requirements of the quick repair specification.

## 2. Procedure for Measuring Work Life and Cure Rates

Samples of base and accelerator were mixed at room temperature for 1 minute and placed in each of 2 polyethylene containers 1/2" deep and 1 1/2" across. One sample was kept at room temperature while the other was exposed in the refrigerator at 40°F. 'Stick' work life was initially determined by measuring the time until the mixed material showed evidence of cross-linking by exhibiting some memory when distended. Usually, the practical working time is 1/2 to 1/3 of this value. For more accurate determinations, samples were quickly mixed, and placed

in Semco polyethylene tubes with 1/8" nozzles and extruded at 90 psi. The end of the practical work life was assumed to be at the point where the extrusion rate fell below 15 grams per minute.

Since in low temperature curing tests for rapidly setting materials, significant time may elapse before the 1/2" mass cools to 40°F -- and this extra heat would improve the cure rate -- a comparison was made with the hardening rate of a 1/8" thick specimen coated onto a mold-released aluminum panel previously cooled and coated in the refrigerator. When the useful application life of the product was greater than 15 minutes, no difference in the cure rate was observed between these two methods. As hardness determinations on thin films are inaccurate, the material was peeled off and folded over for determination of hardness.

### 3. Oxidation Cures of Mercaptan Terminated Polythioethers

Since experience with fast curing versions of dichromate and manganese dioxide cured Thiokol showed they met the general performance requirements of MIL-S-8802, it appeared reasonable to explore the characteristics of Permapol® P-3 with dichromate and manganese dioxide cures, with the expectation that improvements in low temperature curing might be observed. The similarity of the cited structure with Thiokol, -C-C-O-C-O-C-C-SS- vs P-3 (28) -C-C-O-C-C-S-, is evident. A basic formulation was made up using a standard PRC dichromate accelerator 10/1 with a Permapol® P-3 having a molecular weight and functionality nearly identical to that of Thiokol LP-2, about 5000 MW, and average functionality of 2.5.

The following formulation was a basic model:

<u>Base Component</u>	Permapol® P-3	100
	Calcium carbonate (uncoated)	50
<u>Accelerator Component</u>	Calcium Dichromate	7
	Water	8

The room temperature application life with the above accelerator was less than 5 minutes while a similar formula using Thiokol had an application time of several days. The Permapol material at 40°F was well cured in four hours (about 20 rex, but somewhat plastic) and showed surface tack. Excellent overnight cures were obtained.

#### 4. Zinc Oxide Aided Cures

It was observed here that the incorporation of zinc oxide improved the low temperature cure and eliminated the tack. However, there was no place to put the zinc oxide where it would not react since it formed a cured rubber with the mercaptan terminated polymer alone, and insoluble zinc chromate formed when mixed with the dichromate accelerator.

As a short side experiment it was thought that some additives, mainly adhesion promoters could be incorporated which would extend the work life and yet provide low temperature cures. Additives examined included Epon 828 and 1001 epoxies from Shell, reactive phenolic, Durez 126957 and mercapto silane UCC-A-189. No benefits were observed.

Since zinc oxide showed such interesting properties, it was thought that other zinc compounds as well as magnesium oxide might be utilized that would show beneficial properties without the high instability brought about by the zinc oxide. Zinc carbonate and zinc sulfide were tested and found to be more stable but also far less effective.

It was felt that investigation of the dichromate cure of P-3 to extend the work life to a more controllable, longer period, had merit, especially in conjunction with some zinc compound, even if it became necessary that the zinc be incorporated as a third component, since repair applications are generally of low volume and storage stability is paramount. To that end, a series of experiments were undertaken to determine the conditions for lengthening the application life beyond the 5 minutes obtained with standard PRC accelerators.

In one experiment, chromic acid was dispersed and ground in an inert, aromatic hydrocarbon. Zinc oxide was made up into a separate dispersion in the hydrocarbon oil while a third component was the polymer containing calcium carbonate. It was the expectation that the powdered chromic acid would slowly react with the coated zinc oxide making zinc chromate, in situ, and finally curing the material. This did, in fact happen, but the reaction was too localized because of the unsolubilized particles of acid. In all of these experiments, the zinc is expected to finally appear as insoluble zinc sulfide. This would minimize any cathodic interaction with the aluminum.

TABLE II

Effect of Zinc Oxide Concentration  
on Room Temperature Cure Rate of Chromic Acid  
Dispersion Cure of Permapol P-3

	<u>FORMULA NUMBER</u>		
	262-6J	262-6K	262-6L
Base 262-5A	5.2	5.2	5.2
Permapol P-3	2.0	2.0	2.0
Calcium Carbonate	0.3	0.3	0.3
Titanium Dioxide			
Zinc Oxide Dispersion			
Zinc Oxide	1.75	5.3	2.5
Plasticizer			
(Polymer P-3 terminated with an alkyl thioether)	.36	1.1	.725
Dimethyl acetamide	.36	1.1	.725
Chromic Acid Dispersion			
Chromic Acid	.28	.42	.35
Aromatic Oil	.72	1.08	.90
Work Life @ 77°F	60 min	1 min	5 min

The chromic acid dispersion in oil was found to be very dangerous in that spontaneous ignition during preparation can occur.

##### 5. Buffered Chromate-Dichromate Cures

It was found that by using magnesium dichromate, magnesium chromate combinations in water the application life could be extended to two hours. Similar results could be obtained by judicious use of ammonia (or ammonium dichromate). Also reduction of the excess of chromate or dichromate ion over theory gave further extension of work lives.

A typical formulation for accelerator to be used 1/10 with Permapol P-3 containing 50 parts of finely divided calcium carbonate was magnesium dichromate dihydrate - 7 parts; magnesium chromate, pentahydrate, - 40 parts; water - 100 parts. This gave a two hour application life but would not meet the low temperature cure requirement without the introduction of zinc oxide.

TABLE III

Results Obtained With a  
Magnesium Chromate-Dichromate Accelerator  
(1/10 accelerator to Permapol® P-3 base)

Curing System	<u>Work Life</u>	<u>Hardness</u> 4 hrs.	<u>Hardness</u> 16 hrs.
MgCr <sub>2</sub> O <sub>7</sub> , 33% in water	3 minutes	25	40
1 MgCr <sub>2</sub> O <sub>7</sub> , 7MgCrO <sub>4</sub> 33% in water	30 minutes	0	35
1 MgCr <sub>2</sub> O <sub>7</sub> , 7 MgCrO <sub>4</sub> , 1 ZnO in water	10 minutes	20	40

In an effort to improve the work life/cure ratio of dichromate cures, most attempts that gave a satisfactory cure at 40°F gave too short an application life at 77°F for practical purposes. Use of water solutions of the chromate-dichromate mixture, when adjusted to a 15 minute work life gave marginal tacky 40°F cures, at best. When dimethyl formamide was substituted for water and the ratio of the two salts varied, a satisfactory low temperature cure was observed, with, or without zinc oxide, but the application life was too short.

#### 6. Manganese Dioxide Cure of Permapol® P-3

For comparison purposes with the best available material based upon manganese dioxide cures of Thiokol polysulfide, an investigation of the same cure with Permapol® P-3 seemed indicated.

When P-3 was used in a standard Thiokol type formulation where 3 - 5% of reactive phenolic resin is typically present for adhesive purposes, the material showed sluggish cures unless very high concentrations of alkaline manganese dioxide were used -- or strong amines. Even then, the work life to cure ratio was unfavorable. By omitting the phenolic resin which reduces the

adhesion to metals, it was observed that the proper selection of the activity of the manganese dioxide gave work-life cure relationships in a potentially acceptable range. Concurrently, the storage stability of the material would be improved. The basic formulating compound used 100 parts of Permapol® P-3 with 150 parts of calcium carbonate blended with 13 parts of the candidate manganese dioxide dispersed in an aromatic oil. Various tertiary amines were added for further activation.

The manganese dioxides employed ranged in pH from 9 to 11. Fresh batches of the most alkaline accelerators gave an initial stick life of 20 minutes; but one week aging at 120°F caused a drift to 30 minutes with a 20 Shore A hardness after 6 hours at 40°F - rather slow. Polymer variations on these compositions were studied later on in the contract.

#### 7. Two Component Isocyanate Terminated Polythioethers

Work was initiated examining cure rates of other two component systems using the polythioether backbone. Beginning with a hydroxyl terminated polymer similar in functionality, molecular weight, and backbone to the mercaptan terminated Permapol products used so far, toluene diisocyanate was reacted with the hydroxyl groups. Thus in 5000 grams of hydroxyl terminated polymer was added 3 moles of mixed 2,4 and 2,6 toluene diisocyanate along with a trace of tertiary amine catalyst. The mixture was heated at 120°F for 7 days. This type of product could also be considered for one component cures as well as two component. While it could not be expected that the one component type would be applicable in faying surface situations since there is no exposure to the atmosphere, the rapid skinning of these materials could lend itself to certain types of maintenance applications. The isocyanate terminated prepolymers were mixed with various aromatic diamines such as p,p'diaminodiphenyl methane in essentially stoichiometric ratios. Many of the materials cured rather well at 40°F if they were also rapid curing at room temperature but there did not seem to be any unusually favorable relation between room and low temperature cures.

Isocyanate terminated polymers were also prepared using 1,6 hexamethylene diisocyanate. When combining this generally slower curing material with aliphatic amines, a 10 minute gel time was obtained and no way was found to slow down the cure rate. On the other hand, hindered aromatic amines gave more than 3 hours application time at room temperature. A blend of aromatic amine and hydroxyl terminated Permapol P-3 used with isocyanate terminated P-3 gave a work life of 1/2 hour with a soft, tack-free cure in 4 hours at 40°F and a 60 Shore A hardness overnight. The cure however, did not proceed readily at low temperatures. Ketimines also seem capable of controlling the work lives of these materials.

A typical formulation involved hydroxyl terminated P-3, MW 5000 with a functionality of 2.5, candidate diisocyanate 2.5 moles, and prereacted until the hydroxyl band was gone as shown by IR and then adding about two equivalents of candidate curing agent, (amine).

Typical Two Component Isocyanate Terminated  
Permapol P-3 Compound

<u>BASE</u>	
Permapol P-3 (OH terminated) equiv. = 1700	206
p,p'diphenyl methane diisocyanate	32.8

Mix, degas at 30" Hg, and heat 48 hours at 120°F.  
To above add:

<u>ACCELERATOR</u>	
Permapol P-3 (OH terminated) equiv. = 1700	38
Aromatic Diamine equiv. wgt. = 158 (PRC MA-20)	18
Dibutyl Tin Diacetate	1.2

This cured overnight at 120°F to a tough material with excellent fuel and water resistance. Its four hour cure at 40°F was marginal.

8. Epoxy Cures of Mercaptan Terminated Permapol P-3

The reaction of epoxy resins with mercaptan groups is known to exhibit lower exotherms than with amines. On this basis it would appear possible that the difference in rates between low temperature and room temperature cures might be less with such a reaction than with epoxy-amine combinations. In order to confirm this, a one pound sample of Permapol P-3 was mixed with an equivalent amount of DOW epoxy novolac resin DEN 438 in the presence of 1% tertiary amine catalyst. The temperature rise was 15°F, unlike normal epoxy amine reactions which typically exhibit high exotherms with fast curing systems.

A series of formulations were prepared varying the polymer in terms of functionality, presence of urethane groups in the backbone, functionality of the epoxy resin, type and quantity of tertiary amine catalyst type and quantity.

Many of these combinations exhibited relatively long room temperature application lives, frequently greater than 30 minutes, yet seemed to cure firmly to a thermoset rubber in 4-6 hours at 40°F. Most had some surface tack which later disappeared on standing. Softer products were later formulated which incorporated some Permapol P-3 fuel resistant plasticizer and some amine terminated acrylonitrile as a coreactive plasticizer.

Formulations of Mercaptan  
Terminated Permapol® P-3 with Epoxy Cures

<u>Base 262-82A</u>		<u>Accelerator 262-82B</u>	
Permapol® P-3 SH equiv. 1803	400	Epoxy Resin, (DEN 431)	200
Titanium Dioxide	40	Epoxy Resin, (DEN 438-EK85)	200
Calcium Carbonate	280	Carbon Black	40
Phenolic Resin (GE Methylon 75105)	12	Calcium Carbonate	<u>360</u> 800
Tertiary Amine (Dabco 33LV)	<u>6</u> 738		

TABLE IV  
EFFECT OF VARIATION OF EPOXY TO BASE  
RATIO ON CURE RATE AT 40°F

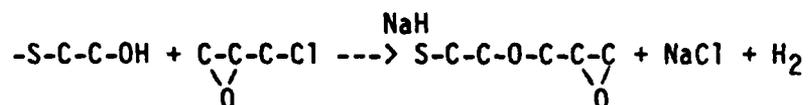
	<u>C</u>	<u>D</u>	<u>E</u>
262-82A Base	50.0	40.0	40.0
262-82B Accel.	10.85	4.0	6.15
Pressure Rupture, 4 hr. +40°F, psi	>34	20	25
Peel (lb/in)	13		
Tensile Strength (PSI)	300		
Elongation (%)	300		
Extrusion Rate (gm/min) @ 10 MIN. 90 PSI	16	16	16
40°F Cure, 4 hrs., Shore A	30	Soft	0

The extrusion rate was not observed to change here with epoxy concentration.

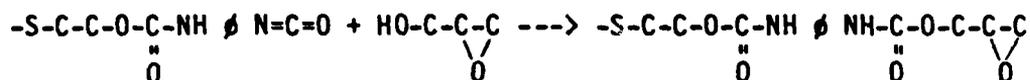
## 9. Preparation of Epoxy Terminated Polythioether

Since the epoxy cure of mercaptans appeared to have a favorable work life/cure relationship, further work was done exploring variations of this approach.

One suggestion was to epoxy terminate the polythioether polymer according to the following reaction:



Several attempts were made but the conversion was only about 60%. The material cured to a very soft rubber when blended with mercaptan terminated polymer in the presence of amine catalyst. An attempt to cap the mercaptan was made by reacting with excess diepoxy (Shell 828). The product was unstable on storage. The activity of the urethane hydrogen with the epoxy groups can result in storage instability. If the isocyanate terminated polymer of the polythioether is reacted with glycidol, a smooth, higher conversion is expected:



No further work was done along these lines, however. Presumably, this epoxy terminated polymer, when combined with an equivalent amount of mercaptan terminated polymer, would convert to a cured elastomer with similar good temperature curing characteristics observed with the lower epoxies and would offer a suitable alternative.

## B. Single Component Systems

## 1. Polyethylene-acrylate Hot Melts

The DuPont company manufactures an ethylene-acrylate terpolymer which has pendant carboxyl groups that can be used to produce hot melts of relatively high resistance to cold flow, and aliphatic hydrocarbons.

Vamac Hot Melt Formulation

VMX 5245 (70% polymer 30% carbon black)	49.4	All ingredients are combined in a heated micro-Banbury mixer until uniform. The silane is added last.
Picco 6140	19.7	
Plastolein 9734	14.8	
Versamid 900	14.8	
Silane A-172	0.3	

The product was applied to metal panels using a Hardman hot melt gun heated to 400°F. It was observed that the material requires a generally higher temperature for satisfactory application than the less heat and fuel resistant butyl rubber 'hot melts'. On cold surfaces the material tends to chill prematurely and not develop full adhesion. The cold material will also not wet itself readily with new hotter material. Samples allowed to stand for several months showed a tendency to pull away from surfaces due to residual shrinkage stresses. Formulations in which additional carbon black was added seemed to decline gradually on aging in rate of adhesion development, due probably to a slow reaction of alkaline sites with the free carboxyl content of the polymer. Exposure of samples to JRF at 140°F resulted in nearly complete solution of the tested formulation, the fuel becoming black and the specimen being seriously attacked.

## 2. Thermoplastic Thiokol Polysulfide

A Thiokol based channel sealant, PR-702 was examined briefly as a potential candidate for a hot melt. The viscosity change with temperature was too small to consider it a 'melt'. Two other disadvantages were evident:

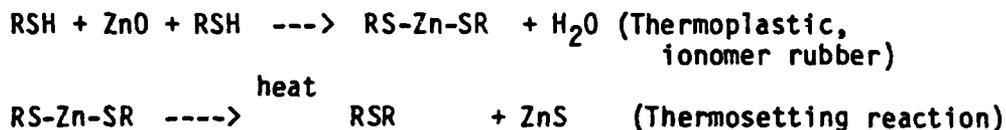
- (a) Thiokol based products on long exposure to temperatures needed for molten extrusion would tend to decompose.
- (b) The particular formula selected does not have enough rigidity over the normal working temperature range to avoid 'blowout' in the specification testing.

### 3. Zinc Oxide Based Ionomers

An interesting material was formulated from Permapol® P-3, wherein the mercaptan terminated polymer was mixed with zinc oxide according to the following:

Permapol® P-3	100
Zinc Oxide	100
Cure Rate 7 hrs. @ 77°F	65 Rex
Cure Rate 7 hrs. @ 40°F	10 Rex

The mixture gave a thermoplastic rubber which melted sharply at 400°F. Exposure of the material to water at 158°F and jet reference fuel at 140°F showed little or no change. However, the material after exposure to 400°F for a number of minutes became thermoset. The reaction is believed to be:



Varying the amount of zinc oxide did not give a stable composition. The monosulfide cured product was a tough rubber of high thermal resistance, surviving many hours at 350 - 400°F. It became increasingly harder and tougher with room temperature aging as the residual zinc salt apparently continued to convert to zinc sulfide. As a potential two component material, the conversion was slow, at low temperature.

### 4. Preparation and Formulation of Silane Terminated Polythioethers

Single component polysiloxane sealants rapidly form thick skins on exposure to atmospheric moisture. While polythioethers are not as permeable to moisture as polysiloxanes, rapid surface skinning to produce a fuel resistant membrane could find applications in some quick repair situations.

A number of routes to the preparation of silane terminated polyethers are available and have been previously developed by Products Research and Chemical Corp. Two reactions chosen here for investigation were:

- (a) The reaction of gamma methacryloxypropyltrimethoxy silane with a mercaptan terminated polymer.
- (b) The reaction of a mercaptan terminated polymer with glycidoxypropyltrimethoxy silane.

In order to obtain sufficiently rapid cures, 0.3% of dibutyl tin diacetate was used as a catalyst and some of the silane ester terminals were hydrolyzed with water (0.2%) to shorten the setting time to one-half hour. Experimental formulas, without fillers, cured to a tack free surface in four hours at 40°F, but were only 10-15 Shore A hardness overnight. The fully cured polymers were extremely "short" and crumbled in the manner of a gum eraser.

Formulas of Silane Terminated Polythioethers

	<u>262-8A</u>	<u>262-8B</u>
Permapol P-3 (mercaptan terminated)	105	105
Gamma Glycidoxy propyl trimethoxy silane	12.5	
Gamma glycidoxy propyl trimethoxy silane		11

262-8A was faster in cure rate when mixed with water and catalyst than was 262-8B. The following formulas were prepared:

TABLE V  
Comparison of Cure Rates of Silane Terminated  
Polythioether Formulations at 40°F

<u>Formula</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>N</u>
Silane Terminated Polymer 262-8A	20	20	20	20	20	20	20
Baysilone Polymer C-50 (polysiloxane)	1	1	1	2	2	2	0
Tetraethyl orthosilicate	.5	.5	.5	.5	1	1	1
Water	.5	.5	.5	.5	1	1	.4
Dibutyl tin diacetate	.1	.4	.6	.6	.2	.4	.06

Only formulas E and F cured sufficiently at 40°F to be considered, but they were too friable to be of value.

This is not surprising when it is recognized that molecules with an initial functionality of 2.5 develop a functionality of 7.5 when prepared in the described manner. Other means are available to reduce or eliminate this tendency utilizing less functional silanes and polymers but no further work was done in this area. It was shown, however, that rapid surface curing materials can be obtained with this technology.

5. Preparation of Isocyanate Terminated Polythioethers and Their Atmospheric Moisture Cures

It has been noted in the field that PR-312, a low gravity, single component sealant for aircraft, cures quite well in the open environment. This material is based upon an isocyanate terminated polyether whose relative permeability to water vapor is high, allowing potentially rapid cures. Its permeability to carbon dioxide (the by-product gas of the cure) is not known but is probably fairly high compared with many other polymers.

If a fuel resistant elastomer based on the same technology were available and if its surface cured in similar rapid fashion, some applications in the quick repair field could be rationalized. With that aim, a large series of formulations involving the isocyanate termination of Permapol P-3, hydroxyl terminated, were prepared and investigated for curing properties. In the initial work, PR-312 was duplicated, without pigment, and simply substituting the diphenyl methylene diisocyanate terminated polythioether glycol for the polypropylene oxide backbone.

Initial Formulation

OH terminated Permapol P-3	568
OH equiv. 1300	
Chlorinated paraffin	39
4, 4'diphenyl methane diisocyanate	120
Dibutyl tin dilaurate (10%)	10

The reaction is carried out after initial degassing at 120°F for 16 hours. This formula showed excessive foaming when exposed to the air.

The isocyanate terminated polymers were poured into gallon polyethylene container lids and allowed to stand in the

laboratory at 77°F and 30% RH, overnight. Nearly complete through cure was observed but the clear material showed masses of bubbles and blisters under the surface up to 2" across. The top 1/32" of the casting was dry, tough, and bubble free. Many formulas exhibited this tack free cured surface after only an hour exposure at room temperature and were similarly cured in the refrigerator at 40°F after 4 hours. A large number of experiments were run in an attempt to eliminate this bubble formation without foregoing the rapid surface cure.

One basic philosophy in formulating "bubble free" one component isocyanate terminated materials involves reducing the quantity of evolved carbon dioxide. This can be achieved by preparing higher molecular weight prepolymers which thereby have a lower

percentage of free isocyanate groups and so yield less gas. When this was done, the viscosity rose to the point where dilution with plasticizer became necessary and storage stability was reduced with this type of formula.

Another approach is to lower the rate at which the gas is evolved. By replacing aromatic isocyanates with aliphatic, gassing is, in fact, reduced but the rate of cure is also so diminished that the material no longer has practical value as a quick repair material.

A third possibility in reducing bubble formation is to increase the solubility or the diffusion rate of carbon dioxide in the system. Polypropylene oxide polymers exhibit much lower levels of gas entrapment than do the polypropylene sulfide polymers. This can be attributed to a difference in solubility and diffusion rates of carbon dioxide between the two polymer types. By adding some oxygenated plasticizers to the system, reduction in bubbles was observed but the material was no longer adequately fuel and water resistant, and it still showed gassing. The following formulas were prepared:  
(See TABLE VI)

TABLE VI  
 Variations in Formulation  
 of Single Component Isocyanate Terminated  
 Permapiol P-3 and Effect on Foaming

<u>Ingredients</u>	<u>262-54</u>	<u>262-56</u>	<u>262-60</u>	<u>262-68</u>	<u>262-75</u>
Permapiol P-3	454	545	131* + 330	500	500
Hydroxyl equiv.	1300	2700	750 + 3000	1760	1430
Alkyl thioether capped Permapiol P-3 plasticizer	---	250	---	---	---
Chlorinated Paraffin	---	---	---	200	---
Magnesium Oxide	---	---	---	---	10
Clay (Novacite 1250)	---	---	---	20	75
Cabosil (silica)	---	---	50	---	---
Aluminum powder (MD 3100)	---	---	---	---	15
4,4'diphenyl methane diisocyanate	96	29	21* + 30	79	96
Trimethyl hexyl diisocyanate	22	---	---	---	---
Polybutylene glycol (polymeg 1000)	---	---	---	---	40
Dibutyl tin dilaurate (10%)	8	2.5	2.7	7.1	8.7
Toluene	250	---	---	---	---

\*The first number was used to prepare a prepolymer.

All materials foamed excessively.



- (b) Use of mono acrylates to eliminate some of the potential branches.

Formulation of an Acrylic Terminated,  
Ultra-Violet Convertible Permapol® P-3

Permapol P-3 (hydroxyl terminated, OH equiv.= 1,500)	100.0
Isocyanato ethyl methacrylate	9.4
Hexyl thioethanol (-OHCH <sub>2</sub> CH <sub>2</sub> -S-C <sub>6</sub> H <sub>13</sub> prereact Isocyanato ethyl methacrylate)	100.0
	102.0
Fibrous polyethylene (Microthene FN 510-00)	30.0
Cabosil HS-5	15.0
Irgacure 651	3.0
	<u>359.4</u>

This material converted to a solid in a 1/8" layer in less than 3 minutes when exposed to sun light.

Both approaches gave better elastomers but materials were still not strong and had deficient elongation. Inclusion of colloidal silica along with fibrous polyethylene gave significantly improved tear resistance without interfering significantly with the ultra violet cure although elongation was reduced. Further work on these systems was not continued since its application is limited to situations where light is available. Further, the lowered fuel resistance encountered with addition of acrylic monomer along with the observed oxygen inhibition indicated further work would not be quickly rewarding.

#### 7. Anaerobic Cures

The higher molecular weight versions of a methacrylic terminated P-3 were briefly examined as potential anaerobic sealants. By putting a thin film of a Schiff's base (reaction of aldehyde and amine) on one metal surface and applying the clear acrylic terminated polymer, peroxide catalyzed, in 10 mil thickness to the other and gently putting the two surfaces together, a cured, rubbery adhesive layer developed in less than one minute. The exudate was uncured and tacky. If Irgacure 651 was included with the polymer, the exudate, on standing became cured in a few minutes outside in the sun, or overnight in the laboratory under fluorescent lights.

This particular approach may be useful in quick patch repairs or in some situations where faying surface sealing requires a long open time and a fast cure. The rate at which the one component anaerobic material sets can be controlled over a wide range by the nature of the catalyst. Storage stability could be of concern with the catalysts employed.

As a result of the initial work on various cure mechanisms, emphasis was now placed on evaluating selected candidate materials for potential development into finished products.

#### IV. PHYSICAL PROPERTIES OF CANDIDATE MATERIALS BEFORE AND AFTER ENVIRONMENTAL EXPOSURES.

##### A. Comparison of Oxidizing Agents and Epoxy Resin as Curing Agents for Permapol® P-3

##### 1. Properties of 2.75 Functional Material

All materials were formulated with polymer containing 28% sulfur by weight, the polymer consisting essentially of two carbon atoms separated alternately, by sulfur and oxygen, with a small percentage of branched methyl groups. Some mercaptan terminated polymers are made with an intermediate isocyanate per U.S. Patent 4,366,307 while others are synthesized by direct condensation to an olefin terminal and later converted to a mercaptan. In the latter case some unreacted hydroxyl groups are present which are sometimes removed by reaction with trace amounts of isocyanate. These are termed 'scavenged'.

The following table VII shows the effect of curing agent variations on the properties of a polymer with a functionality of 2.75. 100 parts of the polymer were blended with 38 parts of precipitated calcium carbonates and 6 parts TiO<sub>2</sub>.

TABLE VII

Effect of Curing Agent on Properties  
of 2.75 Functional Permapol® P-3 (28)

	Alkaline MnO <sub>2</sub> 50% in Aromatic Oil	Magnesium Dichromate 50% in Water	Magnesium Dichromate 50% in Dimethyl Formamide	Epoxy Novolac Dow DEN 438
Parts				
100 parts base	10.0	7.5	7.5	22.0
Elongation %	200.0	300.0	150.0	100.0
Tensile (psi)	285.0	215.0	330.0	305.0
Volume Swell (JRF, 7 days, 140°F)	37.2	5.3	2.6	6.5
Volume Swell (water, 12 days 140°F + 60 hrs 160°F + 6 hrs 180°F)	32.6	1.8	1.8	0.0

The above data indicate that alkaline manganese dioxide, while having a good balance of physical properties initially, suffers excessive swell in fuel and water as compared with the chromate and epoxy cures.

## 2. Properties of Varying Functionality and Modified Backbone Permapol P-3 (28) Cured with Various Agents

The effect of fuel and water immersion on various polymer and curing agent combinations are shown in the accompanying TABLE VIII.

The large difference in results in water swell of the chromates between this series and those of Table VII are apparently due to the fact that only slightly more than equivalent quantities of chromates were used in the first case rather than a two-fold excess per the following equation:



TABLE VIII

SWELLING EFFECT OF WATER AND FUEL IMMERSION ON  
 VARIOUS FUNCTIONAL POLYTHIOETHERS VULCANIZED  
 WITH CANDIDATE MATERIALS  
 7 days 140°F, 3 days 160°F, + 16 hrs. 180°F  
 (Specimens 1/8" X 1/4" X 4")

Polymer Terminal	Functionality	Cure Agent	Further Treatment	Volume % Swell in JRF		Weight Loss	
				Water	Fuel	JRF Fuel	Water
-S-C-C-O-C-N- $\phi$ -NCO H	2.75	H <sub>2</sub> O	None (4.9% fuel soluble plast in base)	15	3	8.5	4.2
-S-C-C-O-C-N- $\phi$ -N-C-O-C- C-C-S-C-C-S-C-C-SH	2.75	MnO <sub>2</sub>	None	11	70	5.2	5.1
-S-C-C-O-C-N- $\phi$ -N-C-O-C- C-C-S-C-C-S-C-C-SH	2.75	Epoxy	None	12	2	3.7	3.2
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.2	MnO <sub>2</sub>	Free OH removed	25	142	4.8	4.0
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.2	Epoxy	Free OH removed	19	5	4.8	1.6
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.75	MnO <sub>2</sub>	None	25	50	5.9	2.9
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.75	Epoxy	None	23	4	3.6	1.0
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.75	MgCr <sub>2</sub> O <sub>7</sub>	None	28	22	4.4	3.9
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.75	MgCrO <sub>4</sub>	None	23	26	5.9	5.0
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.75	MnO <sub>2</sub>	Catalyst removed	24	62	4.7	2.9
-S-C-C-O-C-C <sub>6</sub> -S-C-C-S-C- C-SH	2.75	Epoxy	Catalyst removed	14	10	7.0	3.2

The high fuel swell of MnO<sub>2</sub> cured materials has been eliminated by use of buffered alkaline manganese dioxide accelerators. Results will be reported under contract #N62269-82-C-0370.

The best resistance to fuel and water absorption was exhibited by the epoxy cured materials in these cases.

The heat resistance of the 2.75 functional, urethane-free thioethers cured with manganese dioxide and the epoxy were determined by heating 1/2" X 2" plugs of the cured material at 350°F in a circulating air oven for 3 days with the following results:

<u>EXPOSURE CONDITIONS</u>	<u>WEIGHT AND PHYSICAL CHANGES</u>	
	<u>MnO<sub>2</sub> cure</u>	<u>Epoxy Cure</u>
Open to air at 350°F	-5.7% surface hardening	-5.6% some surface hardening. Internal softening
Wrapped in aluminum foil at 350°F	-2.8% some softening	-2.2%, definite softening

TABLE IX

Hardness and Weight Changes in  
4 Types of Cure of Permapol® P-3 (28)  
on Exposure to Open Air 350°F

<u>Base 262-30</u>	<u>Weight Retention</u>		<u>Hardness</u>	
	<u>1 day</u>	<u>2 days</u>	<u>Initial</u>	<u>2 days</u>
MnO <sub>2</sub> cure	95%	94%	55	60
Epoxy cure	98%	97%	60	70
MgCr <sub>2</sub> O <sub>7</sub> in DMF	92%	---	50	30
MgCrO <sub>4</sub> in H <sub>2</sub> O	94%	---	53	20

It was of interest to examine the properties of the polymers cured with the same catalysts but with the acidic catalyst used in the initial polymerization removed from the system by alkaline washing. When cured with manganese dioxide and epoxy resin as before, no significant change was noted in heat resistance but the cured hardness was somewhat lower with the washed specimens.

### 3. Effect of Reduced Polymer Functionality on Properties

Two mercaptan terminated polymers with a functionality of 2.2 rather than the standard 2.75 were examined for initial physicals and resistance to immersion in fuel and water. The polymers differed in that one had a trace of free hydroxyl while the other had the hydroxyl content removed.

TABLE X

Comparison of Physical Properties of  
2.2 Functional Permapol® P-3 (28), MW 5,000,  
Cured With Manganese Dioxide and Epoxy Novolac

<u>Polymer Modification</u>	<u>Curing Agent</u>	<u>Elongation %</u>	<u>Tensile psi</u>
Hydroxyl present	MnO <sub>2</sub>	700	190
Hydroxyl present	DEN-438 novolac	200	284
No hydroxyl	MnO <sub>2</sub>	600	184
No hydroxyl	DEN-438	200	420

The lower functionality polymers had much higher elongation. The water swell with a manganese dioxide cure of low functional polymer is quite high but this is largely eliminated with the increasing functionality introduced by the triepoxy resin used at the expense, however, of much reduced elongation, but significantly higher tensile strength.

As can be seen in Table VIII, the fuel and water swell of epoxy cured polymers are significantly less than that of alkaline manganese dioxide cured specimens and appears to be even further reduced when a urethane linkage has been introduced. The beneficial influence of the urethane linkage can be estimated from Table VIII without the superimposed variables of curing agent when it is noted that an isocyanate terminated P-3, cured by water exposure, has elongation of 250% and a tensile of 351 PSI along with fuel and water swells of less than 10%.

## V. DEVELOPMENT OF AN EPOXY-PERMAPOL P-3 TWO COMPONENT SEALANT

### A. Effect of Formula Variations on Properties

As a result of the experience with the good low temperature cures obtained with epoxy conversions of mercaptans, a decision was made to concentrate on this reaction. Variations in epoxy level, functionality, and tertiary amine catalyst were conducted with the

initial aim of optimizing the cure rate relations at room temperature and 40°F. (See TABLE IV)

As a result of experience with epoxy Permapol® P-3, the following formulation was decided upon for initial submittal:

Experimental Formulation 262-88

<u>Base</u>		<u>Accelerator</u>	
Polythioether Polymer	100.00	Epoxy Resin (Dow DEN 438 (85) func. 3.8 Epoxy equiv. 205)	21.75
(SH equiv. 1807, func. 2.75)			
Titanium Dioxide	10.00	Calcium Carbonate	15.28
Calcium Carbonate	70.00	Carbon Black	<u>2.17</u>
			39.20
Phenolic Resin (GE Methylon 75105)	3.00		
Dabco 33 LV	<u>1.25</u>		
	184.25		

This formula had a relatively high viscosity initially, and a good cure rate at 40°F. This formula showed a satisfactory work life at room temperature and was later modified by the inclusion of three percent by weight of toluene and omission of the calcium carbonate from the accelerator. Samples of this modification were submitted but did not show proper low temperature cure. The solvent apparently slowed down the cure rate here.

Properties of Experimental Formulation 262-88

<u>Paragraph</u>	<u>Test</u>	<u>Performance Specification</u>	<u>Observed</u>
3.4.1	Application time, gm/min @ 10 minutes	15	22
3.4.2	Cure Rate (4 hrs 40°F) hardness	12 (6 hrs)	20
	Pressure rupture, psi (4 hrs., 40°F)	28 (6 hrs)	34+
3.4.3.1	Nonvolatile content, %	92	98
3.4.3.2	Flow, inches	0.1-0.75	0
3.4.3.3	Specific gravity	<1.65	1.5
3.4.3.4	Peel strength, pli initial	15	13
	After 7 days in JRF at 140°F	15	2 (cohesive failure)
3.4.3.5	Tensile strength, psi	200	300
	Elongation, %	150	200

Peel strength after exposure to JRF was very low. The material after initial preparation showed a short period of 'aging' during which time its cure rate fell somewhat but remained within the target envelope. Aging changes did not continue. Formulations 330-45D and 330-45F do not show low peel strength after heat or fuel exposure. (See Page 32)

#### B. Adhesion Investigations

The basic formulation of epoxy and polythioether exhibits adhesion to a number of surfaces, but the rate of development is variable depending upon the method of application, cleanliness, temperature, etc. Initial consideration was given to incorporating additional adhesion promoters in the sealant. Epoxy silane was investigated and gave some benefit. It was felt that the time and effort to find a suitable additive that would not disturb the already demonstrated good curing qualities could best be avoided by demonstrating good adhesion with a suitable primer. To that end 2" X 6" panels of surfaces encountered in aircraft manufacture were prepared and covered with an approximate 3/16" layer of sealant composition applied by troweling with a spatula. Primers (not MIL finishes) were allowed to dry 10 minutes. Sealants were allowed to cure overnight before attempting to peel specimens with a knife. Results were also obtained at 40°F and were generally similar but adhesion development was slower.

TABLE XI

Adhesion After 16 Hours at 77°F of  
262-88 to Various Aircraft Surfaces Treated  
with Different Surface Preparations

<u>Surface</u>	<u>Solvent Wipe</u>	<u>(Titanate) PR-148</u>	<u>(Titanate) PR-146</u>	<u>(Silane) PR-142</u>	<u>Ajax Scrub</u>
Alclad Aluminum	None	None	Trying	OK	OK
Anodized Aluminum (MIL A-8625)	OK	OK	OK	OK	OK
Alodine Aluminum (MIL A-5541)	Trying	Trying	Trying	OK	OK
Stainless Steel (MIL S5059)	None	None	None	OK	OK
Titanium (MIL T 69046)	None	Trying	Trying	OK	OK
MIL C 8337 coating	OK			OK	
MIL C 27725 coating	OK			OK	

Similar adhesion results were obtained with a later developed, softer formula, RW-1815-71, although adhesion time was a little longer (not necessarily as long as 16 hours, however). The organic coatings may be used as primers where appropriate, but their curing time is generally several hours or longer. The simplest effective surface preparation was a gentle rub with Ajax cleanser. This aid did not visibly scratch any of the surfaces examined and seemed to ensure good results. PR-142 was about equivalent. Other sealant variations gave similar results with PR-142. Generally the nature of the surface seemed to be the overriding factor rather than the specific formulation examined.

#### C. Formulation of Softer Epoxy-Permapol P-3 (28) Sealants

An area of performance where experimental formula 262-88 was found deficient was in peel strength after JRF exposure. It was decided to prepare a softer formulation which might show better peel after exposure. To that end a large amount of formulating work was carried out to produce a softer material which would still show good low temperature activity. Also since 262-88 had a large excess of epoxy groups, it was felt that a product with a stoichiometric relation between epoxy and mercaptan would show less changes. The accompanying formulations cover some of the work. (See TABLE XII)

In general, incorporation of a fuel resistant plasticizer which has the same backbone composition as the polymer but with terminal ether groups along with a percentage of amine terminated butadiene-acrylonitrile did produce softer, higher elongation products. The ratio of epoxy groups to mercaptan (and amine) groups was brought near equivalency. Actually best results seem to be obtained with about a 15% deficiency in epoxy. Easier application was also obtained with the plasticized materials. One product for sampling was RW-1815-71. Twelve 6 oz. cartridges were submitted for examination. The formula and initial properties obtained are as shown.

Formulas 262-88 and RW-1815-71 gave evidence of decrease in tear and peel strength after heat aging at 200°F. Modified formulas, with reduced epoxy cross-link density, did not reveal this effect. See formulas 330-45D and 330-45F.

FORMULATION RW-1815-71

<u>BASE</u>		<u>ACCELERATOR</u>	
Polythioether Polymer SH equiv. 1911, Func. 2.75	100.0	Epoxy Resin, DEN 438 (EK 85)	19.5
Amine Terminated Butadiene-acrylonitrile ATBN 1300 X 16	52.7	Plasticizer, Permapol® 860	6.0
Amine Catalyst Dabco 33LV	5.7	Carbon Black	2.25
Titanium Dioxide	22.9	Calcium Carbonate	9.75
Calcium Carbonate	133.0		<u>37.50</u>
Thixotropic Agent Thixotrol ST	0.6		
Plasticizer, fuel resistant Permapol® P-860	49.0		
Toluene	<u>11.0</u>		
	<u>374.9</u>		

Properties:

Application Time, gm/min. @ 77°F @ 10 min.	30
Cure Rate 77°F	1 hr. 15 min. firm
Hardness, 20 hr., RT, Shore A	48
4 hrs. 40°F, Shore A	28
Ultimate Hardness, Shore A	57
Volatile Content, %	3
Tear Strength, Die C #/inch	48
Tensile Strength, psi	281
Elongation, %	150

TABLE XII  
 MODEL EPOXY FORMULATIONS SHOWING RELATION  
 OF COMPOSITION TO PROPERTIES

<u>BASE</u>	<u>"A"</u>	<u>"B"</u>	<u>"C"</u>	<u>"D"</u>	<u>"E"</u>	<u>"F"</u>	<u>"G"</u>	<u>"H"</u>
Permapol® P-3 (mercap. equiv. 1807)	40.7	25.2	33.7	38.1	30.2	28.5	27.0	23.4
ATBN 1300X16 AEW952	13.3	5.9	2.2	16.0	15.1	14.2	12.3	---
DABCO 33LV	0.5	0.6	0.6	0.5	0.8	0.7	0.7	0.6
<u>ACCELERATOR</u>								
DEN 438 (EK 85) Epoxy (average equiv. weight, 178.5)	$\frac{8.8}{50.0}$	$\frac{10.9}{50.0}$	$\frac{9.8}{50.0}$	$\frac{9.2}{50.0}$	$\frac{3.0}{50.0}$	$\frac{5.7}{50.0}$	$\frac{8.1}{50.0}$	$\frac{13.7}{50.0}$
<u>2 DAYS AT ROOM TEMPERATURE</u>								
Hardness, Shore A	21	54	37	29	11	41	53	49
Tear #/in.	8.9	30	23	19	9	41	39	36
Tensile, psi	60	254	167	102	41	198	272	193
% Elongation	193	123	187	198	204	180	130	172

FORMULATIONS MODIFIED FOR IMPROVED RETENTION  
OF PHYSICALS AT ELEVATED TEMPERATURE

<u>BASE</u>	<u>330-45 D</u>	<u>330-45 F</u>
Polythioether Polymer SH equivalent 1927, Func. 2.75	100	100
Amine Terminated Butadiene Acrylonitrile ATBN 1300X (825 equiv. wgt)	10	---
Titanium Dioxide	10	10
Calcium Carbonate	50	50
Methanol	3	3
Amine Catalyst Dabco/33 LV	$\frac{5}{178}$	$\frac{5}{168}$
<u>ACCELERATOR</u>		
Epoxy Resin (Dow Novolac DEN 431)	12.5	10
Calcium Carbonate	2.0	1.5
Carbon Black	$\frac{.2}{14.7}$	$\frac{.15}{11.65}$
<u>Properties</u>		
Application Time (Stick Work Life)	40 minutes	40 minutes
Cure Rate at 77°F	1 hr. 30 min. 30 Rex	1 hr. 30 min. 30 Rex
at 40°F	2 1/2 hours 30 Shore A	2 1/2 hours 35 Shore A
Final Hardness	40 Shore A	47 Shore A
Hardness After Aging 2 weeks at 200°F	55 Shore A	50 Shore A
Flexibility, 180 degree bend 3/16" check specimen after heating 2 weeks @ 200°F	no cracking passes	no cracking passes

Since 262-88, the initial submittal has a much higher hardness, it might not show adequate low temperature flexibility. Both 262-88 and the softer RW-1815-71 were applied to primed PR-142 anodized panels and bent at -60°F according to MIL-S-85420 paragraph 4.8.10. Both materials bent without cracking or adhesion loss at -60°F.

## VI. CONCLUSIONS

Investigation of a wide range of one component and two component chemical reactions involving polythioether backbones showed that the reaction of the mercaptan terminated polythioether with epoxy resins give products of good room temperature application lives along with relatively rapid cures at 40°F. Storage stability has been found to be excellent. Formulations incorporating this chemistry have been prepared and submitted to the Naval Laboratories at Warminster and appear capable generally of meeting the application and performance criteria set forth in target specification MIL S-85420 (AS).

## VII FUTURE WORK

Isocyanate terminated polythioethers cured with amines or amine-polyol mixtures have merit as tough, fuel and water resistant films and sealants.

The use of zinc-ionomer salts as rapid setting hot melts would be useful if a way could be found to delay or prevent the change of the salt to a thermoset conditions.

Further exploration of epoxy-mercaptan reactions to exploit the favorable work-life/cure relationships found is indicated. Epoxy terminated polythioethers may have utility here.

RAW MATERIAL SUPPLIERS

Aluminum Powder MD-7100	Alcan
Amine Terminated Butadiene-Nitrile	Goodrich
Ammonium Dichromate	Van Waters & Rogers
Aromatic Oil	Sun Oil
Aromatic Diamine MA-20	PRC
Baysilone Polymer C-50	Mobay
Calcium Carbonate, fine	Solvay
Calcium Carbonate, fine coated	Shiraishi Kogyo Kaishi Ltd.
Calcium Dichromate	Baker Industries
Carbon Black, Raven	Cities Services
Chlorinated Paraffin, (55% CL)	Neville
Chromic Acid	Diamond Shamrock
Dibutyl Tin Diacetate	M & T Chemical
Dibutyl Tin Dilaurate	Interstab
Diaminodiphenylmethane, (MDA)	Olin
Dimethyl Acetamide	DuPont
Dimethyl Formamide	DuPont
Diphenylmethanediisocyanate, (MDI)	Upjohn
Epon 828	Shell Chemical
Epon 1001	Shell Chemical
Epoxy Novalac, DEN 431	DOW
Epoxy Novalac, DEN 438	DOW
Fibrous Polyethylene, (FN510-00)	U.S. Industrial Chemical Co.
Gamma-methacryloxypropyltrimethoxy Silane, (A174)	Union Carbide
Glycidoxypropyltrimethoxy Silane, (A187)	Union Carbide
Hexylthioethanol	PRC
Irgacure 651	Ciba-Geigy
Isocyanato Ethylmethacrylate	DOW
Magnesium Chromate	U.S. Mica
Magnesium Dichromate	PRC
Magnesium Oxide	Merck
Manganese Dioxide, (9.2 pH)	Shepherd Chemical
Manganese Dioxide (10.5 pH)	Hoechst
Mercaptopropyltrimethoxy Silane, (A189)	Union Carbide
Permapol® P-3 Plasticizer P-815	PRC
Permapol® P-3 SH Terminated P-810	PRC

RAW MATERIAL LIST (Cont.)

Permapol® P-3 OH Terminated P-855	PRC
Phenolic Resin (Methylon 75105)	General Electric
Picco 6140	Hercules
Plastolein 9734	Emery Ind.
Polybutylene Glycol, (Polymeg 1000)	DuPont
Silica, (HS-5)	Cabot
Tertiary Amine, (Dabco LV 33)	Air Products Chemical
Tetraethylorthosilicate	Union Carbide
Thiokol, (LP-2)	Morton-Thiokol Corp.
Titanium Dioxide	DuPont
Toluene	Union Oil
Toluene Diisocyanate	Mobay
Vamac, (VMX 5245)	DuPont
Versamid 900	Henkel
Vinyl-Tris-(beta-methoxyethoxy)	Union Carbide
Silane, (A172)	
Zinc Oxide	Gulf & Western

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