CR 137706

HUGHES REPORT NO. P75-223

```
(NASA-CR-137706)   DEVELOPMENT  OF AN                 N75-28228
OPTIMIZED  INTUMESCENT  COATING   Summary
Report  (Hughes  Aircraft  Co.)   92  p  HC  $4.75
                                        CSCL  11C        Unclas
                                               G3/27   29073
```

Summary Report
Contract No. NAS-2-8139

DEVELOPMENT OF AN OPTIMIZED INTUMESCENT COATING

Norman Bilow
Seymour S. Schwartz

JULY 1975

AEROSPACE GROUPS
HUGHES
HUGHES AIRCRAFT COMPANY
CULVER CITY, CALIFORNIA

CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

FOREWORD

This report describes the work performed by Hughes Aircraft Company under NASA contract 2-8139. Work was performed during the period April 1, 1974 through February 28, 1975. The contract was sponsored by the Chemical Research Projects Office of NASA Ames Research Center and Mr. S. R. Riccitiello served as the NASA Project Monitor.

The Hughes program manager was Dr. Norman Bilow, Senior Scientist, Advanced Technology Laboratory. His principal coworker was Mr. Seymour S. Schwartz. Technical assistance was also obtained from Dr. R. E. Kelchner, Mr. Harry Schwartz, Mr. Jack Hoffman, Mr. Thurman Saxer and Mr. Jeff Lohof.

I. ABSTRACT

Research on improved intumescent coatings for relatively small diameter Navy air-launched missiles (i. e., 5" to 14" in diameter) has resulted in the development of an aerodynamically smooth, moderately flexible coating, with excellent thermal efficiency. The coating is in the form of molded sheets which can be bonded to the missile surface using additional uncured coating or other suitable adhesive.

The material, designated M30, is a modification of the NASA-313 formula, wherein Johns-Manville Microquartz fibers are used as a substitute for Refrasil fibers, wherein the polysulfide to epoxy weight ratio is 1.25:1 rather than 1:1, wherein the catalyst content is reduced (2.5 weight percent), and wherein the solvent is eliminated. The resultant coating is a superior material.

Work was conducted in three phases. In Phase I efforts were directed to the development of a smooth coating by changing application techniques/or making formulation changes. In Phase II, formulations were investigated containing potentially more thermally efficient, less expensive intumescent salts which were less exothermic and which evolved lesser quantities of combustible breakdown products. Phase III, commenced upon completion of the other two phases, had as its goals, the formulation of test batches of the optimized material, coating of hardware and development of a material and application specification.

Of the various intumescent agents evaluated, only four gave coatings with good thermal efficiency. These included (1) N, N'-bis(4-nitrophenyl) sulfamide, (2) 4-nitroaniline-2-sulfonic acid ammonium salt, (3) N, N', N''-tris(2-sulfo-4-nitrophenyl)-2, 4, 6-triamino-1, 3, 5-triazine triammonium

salt, and (4) the m-phenylenediamine salt of 4-nitroaniline-2-sulfonic acid. The first of these compounds was ultimately rejected because of its hydrolytic instability, the third compound was rejected because it was more costly than the second and had no evident advantage over the second, and the last of the four was rejected because it induced gelation of the coatings in which it was incorporated. The second agent thus was the agent of choice.

Various polysulfides were evaluated, but none were more effective than LP-3. Solventless coatings were studied in order to produce castable and moldable coatings. Microquartz fibers were evaluated in an effort to provide sprayable coatings wherein the fiber would not interfere with the coating flow properties and provide a smoother coating; however, it was subsequently discovered that these fine fibers provided improved char properties.

Phase II was terminated early because the formulations investigated did not produce improved thermal efficiency. Completion of Phase I resulted in the development of an optimized coating and an application process. Both product and process were developed further during Phase III. Batches of the optimized coating were made and sheets were fabricated utilizing manufacturing processes developed during the program. Fabricated sheets of the optimized material were applied to test panels and cylinders for evaluation. Test results demonstrated that the smoother coating had much improved thermal efficiency over earlier formulations of NASA-313. Application processes developed, although preliminary, demonstrated that the system can be applied to missile hardware. A process specification for the material has been written. It is recommended that a pilot production scale up effort be conducted to finalize the material and processes for retrofit to Navy missile systems.

II. INTRODUCTION

Intumescent coatings are coatings which swell markedly upon heating and such materials have been found to be useful as fire retardants. In the better intumescent coatings, protection is achieved via the formation of a carbonaceous porous matrix which functions as a thermal barrier. Simultaneously, flame-quenching, gaseous breakdown products are produced during the degradation process. The best coating of this type is one designated NASA-313. This coating was developed by P. Sawko, J. Parker, S. Riccitiello, G. Fohlen, R. Griffin and E. Fontes of the NASA Ames Research Center, Moffett Field, California; it is the coating which is the basis of comparison in the work described herein.

Intumescent coatings such as NASA-313 can increase the time required for a fire to cause detonation of a missile from 20-30 seconds to 3-5 minutes. Thus, this is an important application for intumescent coatings and is the specific application for the coatings which are the subject of this report.

The project had two principal purposes, namely, the development of a modified version of the NASA-313 coating which was specifically developed for small diameter missiles and the development of appropriate application procedures, and specifications (as specified in statement of work, Material and Process). The coating to be produced was to be aerodynamically smooth, have a low exotherm at the intumescent temperature, not evolve combustible gaseous degradation products during intumescence, be cost-effective, have a high thermal efficiency, good resiliency, and easy application. These objectives were to be achieved by modifications in the ratio of constituents, by the replacement of the intumescent agent with other intumescent agents if necessary, and/or by replacement of the fiber reinforcement using NASA-313 as a basis of comparison. Each of these concepts was explored. Also studied were various new coating production and application procedures.

This report is divided into three phases which are discussed in sequence in the report. In the first part of Phase I efforts were made to develop improved methods for applying NASA-313 to obtain smooth surface finishes and in the second part of Phase I, formula modification studies were conducted using NASA-313 as a basic formula, and modifying the ingredient proportions or introducing analogous substitute materials. Phase II of the study dealt with coatings containing entirely new intumescent agents or entirely different types of polymeric binders. In Phase III, the best Hughes coating was prepared in sufficient quantity to allow comprehensive qualification tests to be made and to allow hardware application demonstrations to be performed.

It will be noted that under Phase II of the technical discussion only the four best intumescent agents are discussed. Others were studied, but because of their poor performance they are discussed in Appendix I.

Following the technical discussion is Section IV of the report designated "Conclusions" and this in turn is followed by Recommendations (V), References (VI), Appendix 1 (VII) which describes the synthesis of compounds which proved to be of little or no value as intumescent compounds, and finally Appendix 2 (VIII) which is a process specification.

Prior to conducting the work described herein, the Hughes Aircraft Company carried out two other intumescent coating investigations, also under NASA sponsorship. The first of these investigations involved a study of coatings containing the intumescent compound 4-nitroaniline-2-sulfonic acid ammonium salt. In this initial study (NAS 2-5886), the polymeric binders were varied to provide matrices with various crosslink densities. The binders included amine-cured epoxy resins, polyurethanes, polyamide-cured epoxy resins, polyesters, and furan resins. The purpose of this study was to correlate intumescent efficiency with crosslink density, polymer glass transition temperature (1st and 2nd order), intumescent temperature, melt viscosity and other fundamental parameters.

Subsequently, a program (NAS 2-6387) was carried out to develop optimum processing parameters for the production of NASA-313. This project involved the study of mixing and milling procedures, shelf life, packaging requirements, qualification testing, hardware coating techniques and other parameters which affect producibility. To achieve the program objectives, all materials were analyzed to verify that they met specifications. Various production methods were studied for preparing the various parts of the coating. For example, Koruma milling, stud milling, Ystral milling and ball milling were all compared as salt grinding methods and ball milling was found to be most satisfactory. Storageability was also studied and these tests showed that unlined tinned cans were totally unacceptable, and that glass jars were preferred even over resin coated tinned containers. Such problems as gelation upon storage also had to be resolved. This problem was observed in containers with a large air ullage. Once the problems of composition, blending, and storage were resolved, coating diluents, and coating application methods were studied. Upon completion of these studies, several plywood panels and one fuel hose were coated with the 45B3 formula and delivered to the NASA Project Monitor.

III. TECHNICAL APPROACH

A. APPROACH TO THE PROBLEM

This study was approached in several ways. In one approach efforts were made to develop a smooth intumescent coating by improving application methods of NASA 313 coating, or by reformulation. Coating reformulation studies were found to be necessary and such studies therefore were conducted. In another approach a literature survey was conducted to identify prospective new intumescent agents which were prepared and compared to the agent currently used in NASA 313. After an improved coating was developed application procedures were further optimized and an in-depth coating evaluation study was performed. The work was divided into the three phases discussed below.

B. WORK PERFORMED

1. Phase I - Smooth Coating Development

a. Objective of Phase I

This phase of the investigation was directed toward the development of an aerodynamically smooth intumescent coating and improved techniques for application.

Prior to initiating this task it was decided to determine whether raw materials and component solutions were available from a previous Hughes contract with Furane Plastics, Inc. Contact with the company revealed the availability of approximately 25 gallons of old NASA-313 Part A (which was semi-gelled), some 20 to 25 pounds of Refrasil fibers and a small volume of packaged Part B (epoxy/toluene) and Part C (DMP/toluene). Arrangements were made to procure all of these materials from Furane, at no cost to the contract.

In subsequent tests made to determine the feasibility of recovering p-NASA salt from the gelled polysulfide-salt mixture, it was found that the water-soluble salt could be separated from the polysulfide by simple hot water washing. On cooling, the salt crystallized out. The yield using this process was only 34 percent and the recovery did not appear to be practical. The study was necessitated because of a delay in obtaining new p-NASA$\cdot NH_3$ salt from the supplier (Nyanza Inc., Ashland, Massachusetts).

b. Preparation of NASA-313 Control Materials

Several batches of NASA-313 material were prepared for use as controls. These samples were prepared in accordance with the standard NASA-313 formula shown below in Table 1.

Sandblasted steel test panels 7.6 x 7.6 x 0.158 cm (3 x 3 x 0.062 in.) were spray coated with the NASA-313 material to an approximate thickness of 1.58 mm (62 mils). After a minimum 72 hour air dry and 16 hours at 72°C, (160°F), two types of thermal tests were made on the various batches of control material. One of these tests was a simple thermal expansion measurement made after a 660°F exposure and the second was a thermal efficiency test made under quartz lamps at 10 BTU/ft^2/sec.

10 BTU/ft^2/sec.

TABLE 1. NASA-313 FORMULA

		p.b.w.
Part A	Polysulfide - LP-3	10.7
	p-NASA$\cdot NH_3$	43.3
	Methyl ethyl ketone	22.0
	Refrasil fibers	5.5
Part B	Epon 828	10.7
	Toluene	3.6
Part C	Tris(dimethylaminomethyl)-phenol (DMP-30)	2.1
	Toluene	2.1

The initial batches of material, mixed in tin cans, all exhibited low thermal efficiencies, ranging from ~28 sec/mm to ~47 sec/mm. The linear expansion tests were likewise low, ranging from 25X to 40X. When a change was made to glass mixing vessels, this resulted in thermal efficiencies of 79 sec/mm and 73 sec/mm and expansion ratios of 62X and 54X for the two batches prepared. Tin catalyzed air oxidation of the polysulfide, even for short periods of time during the mixing process, evidently was responsible for this problem. Consequently, all further mixing was performed in glass, stainless steel or plastic containers with uniformly satisfactory results. Materials were all qualified by chemical analysis prior to proceeding with further work.

c. Modified Application Techniques

(1) Direct Spray Deposition of Bondable Coatings. The initial spraying tests were made with the standard NASA-313 formula in which varying concentrations of Refrasil fibers were mixed in a laboratory type "Lightin" mixer (simple propeller mixer). The resultant coatings were invariably somewhat rough and non-homogeneous, regardless of the type of sprayer used and regardless of the amount of fiber or diluent used. Since smooth coatings could not be obtained by direct spraying, tests were made to determine the feasibility of producing sprayed NASA-313 coatings which could later be applied by adhesive bonding. The technique consisted of spraying the coating onto a Teflon-TFE or Mylar film (approximately 1.27 mil thick), allowing it to air dry, then peeling it off. The interfacial surfaces produced in this manner were found to be very smooth, accurately mirroring the smooth plastic film surface. The approximately 1.5 mm thick coating could then be bonded to steel substrates with additional uncured coating or other heat resistant adhesive, leaving the smooth side out. This resulted in an extremely smooth exterior surface. This technique was also tried with cast coatings with similar results.

A change then was made in that the material, with the fiber mixed in, was ball-milled overnight, after which the catalyst was added. A considerable improvement in coating smoothness was noted, with no gross effect on thermal efficiency or thermal expansion as evidenced by simple screening tests on a hot plate with an infrared lamp overhead.

(2) Adhesive Bonding of Pre-Sprayed Coatings. At this point tests were made with Haven Chemical Co. Epiphen 825A, a previously tested heat resistant epoxy-phenolic adhesive, to determine if it was a satisfactory bonding agent. Tests on small, coated plates held vertically in a 349°C (660°F) oven, showed that no slippage or interference with intumescent action occurred. This adhesive was accordingly adopted for use during these initial tests. Later it was found that seams filled with the adhesive would inhibit the intumescent coating from covering the seams. Consequently, uncured solventless coating material, described below, was used thereafter as the bonding agent, with excellent results.

(3) Spray-And-Wrap Technique. Another technique investigated consisted of wrapping polyethylene, or Teflon FEP film, around a coating sprayed on a cylindrical substrate. Smooth coatings are obtained with this technique; however, a considerable amount of care and skill is required since the process consists of the following steps.

1. Spray and allow the coating to set until virtually all the solvent is evaporated and the coating has started to gel.
2. Wrap the plastic film around the cylinder, with a minimum of wrinkles.
3. Rub the film with a Teflon squeegee until a smooth surface is obtained.
4. Allow time to complete the cure, and then remove the plastic film.

The drawbacks in the above process are mainly in the operator skill and judgment required to select the correct moment to apply the film, and the difficulty in application of a wrinkle-free plastic film over a full-size missile body. If the film is applied too soon, solvent entrapment occurs, and this can cause wrinkles in the film and possibly in the coating. If the film is applied too late, the coating may be too hard to smoothen. Thus, while feasible for low quantity production, the technique is not considered highly practical for high quality production.

(4) Precured Sheets. Efforts also were expended on the precured, curved sheet concept. It had previously been found that the standard NASA-313 formulation could be cast or sprayed onto a sheet of Teflon or

Mylar and then allowed to cure almost completely, after which it was turned over (to expose the very smooth surface), and allowed to cure completely on a 5-inch diameter surface. This results in the formation of a curved sheet with a very smooth outer surface. This sheet can then be bonded onto the metal tube with a high temperature adhesive of the type previously described.

The disadvantages of this process are similar to those found with the spray and wrap technique. The material must be turned over and curved at just the right moment; i. e., too soon and the smooth surface is disturbed when the plastic film is removed, too late and the sheet might crack when being curved. While this process is not quite as dependent on operator skill as the spray-and-wrap technique, it still is somewhat more operator-dependent than is desirable. It does have one important advantage in that sheets may be cast to the required thickness and bonded with considerably less operator time and labor than by the conventional spraying technique. However, casting to the required thickness is still not entirely free from operator skill requirements since, with the high percentage of solvent in the NASA-313 formulation, shrinkage is not entirely predictable.

d. Formula Modification Studies

(1) Change of Reinforcement Fibers. In addition to making improvements in surface smoothness, it was also an objective of the program to increase the flexibility of the formulation, without changing the intumescent properties, without promoting increased sagging, and without decreasing the thermal efficiency. One change which could be made easily was the substitution of a smaller diameter fiber for the Refrasil fiber which is currently used in the NASA-313 formula. It was reasoned that the smaller fiber should result in a smoother coating by interfering less with vehicle flow and possibly also result in improved flexibility. The first new fiber selected for test was Johns-Manville code 108 Microquartz with this selection being made because these were the smallest diameter fibers available.

Initial tests on the substitution of this fiber for Refrasil indicated that considerably less Microquartz could be incorporated into the formula than the 7.3 percent (by weight) of Refrasil used in the standard 313 formulation.

When mixed in with the "Lightnin" mixer, approximately 1.5 percent by weight appeared to be the maximum which could be used in sprayable formulations. Subsequently the sprayable formulations all contained approximately 1 to 1.25 percent by weight of Microquartz. These formulations, although smoother, did not appear noticeably more flexible than NASA-313 of similar thickness.

One formulation was prepared by hand mixing using a mortar and pestle in which the Microquartz was added to a weight content of 4.3 percent. The resulting material was putty-like in consistency. This formulation was intended to be applied by troweling or used as a grout for filling cracks. The grout was tested as follows.

Two 7.6 x 7.6 cm (3 x 3 inch) metal test plates were sprayed with a modified NASA-313 coating, which contained approximately 1 percent of Microquartz in place of Refrasil. Before cure was complete, each coating was scratched with a Q-tip stick so as to form two intersecting lines approximately 0.16 cm (1/16 inch) wide in two directions across the test sample. A day later, after the coating had cured to a hard condition, the "cracks" were filled with the grout. On thermal testing of these samples, the material intumesced completely over the cracks, with no discernible signs of the cracks and no indication that two different formulations were used. This indicated that formulations with higher than 1.25 percent of Microquartz would intumesce satisfactorily. However, a better technique than hand mixing had to be found to make such coatings, and a 3 roll paint mill was found satisfactory for this operation.

(2) Flexibilized Epoxies. As previously mentioned one of the major objectives of this program was to develop a formula which would be flexible enough to bend over a 1 inch diameter mandrel. The change in the reinforcement appeared to give some increase in flexibility, but not enough to give a completely satisfactory product. Consequently, a number of techniques for flexibilization was investigated. Among them was one which involved the use of a flexibilized epoxy binder, instead of the more rigid Epon 828, or a combination of the flexibilized epoxy with Epon 828. The flexible epoxy prepolymer selected for evaluation was Dow Chemical Co. DER 732. The mixtures included one with a 15:1 equivalent weight ratio of Epon 828 to DER 732 (M-7), and one with a 9.7 equivalent weight ratio of Epon 828 to

DER 732 (Formulation M-8). In both cases the materials showed poor flexibility. Another formulation was made in which the Epon 828 was replaced entirely by DER 732 (formulation M-11). This formulation was slightly tacky after cure, and showed poor thermal efficiency as shown in Table 2. Thus, further work with flexibilized epoxies was discontinued in favor of work with various molecular weight polysulfides, since this was an alternate approach to the solution of the flexibility problem. The latter study is discussed below.

(3) Variations in Polysulfides. In another effort to produce a more flexible coating, a number of formulations were made using several higher molecular weight polysulfides, LP-12, LP-31, and LP-33, in varying proportions and combinations. Here also it was considered that the higher molecular weight chains would provide more flexible coatings since the cross link density of derivative coatings would be lower than the cross link density of LP-3 based coatings. Initial formulations made using ratios such as 72.5 eq percent of LP-3 and 27.5 eq percent of LP-31 or LP-12 did not yield noticeable increases in flexibility, nor were the thermal efficiencies satisfactory. The composition of these formulations are shown in Table 3 which also includes the thermal efficiency test results.

Inasmuch as the intumescent formulations employing the substitute polysulfides did not appear to be more flexible than the standard NASA-313 in bend tests, new formulations were made with only LP-3 and epoxy in varying weight ratios. In these mixtures the polysulfide-to-epoxy weight ratio was varied from the 1:1 (used in NASA-313) to a weight ratio as high as 2:1. The higher percentage of the LP-3, it was reasoned, would act as a plasticizer by reducing the cross link density thus increasing flexibility. This was definitely found to be true, as shown by simple bend tests. These coatings and their hardnesses, after an overnight 160°F cure, are shown in Table 4. The hardness data is also shown in Figure 1 which incidentally also contains hardness data on various other epoxy-polysulfides also shown in Table 4. In general, the LP-3 was the most satisfactory with regard to flexibility and hardness.

TABLE 2. COATINGS CONTAINING A "FLEXIBILIZING" EPOXY

Components and Formulation	Standard NASA-313			M-7			M-8			M-11		
	gm	eq	Wt[1] %	gm	eq	Wt %	gm	eq	Wt %	gm	eq	Wt %
LP-3	10.7	0.022	15	11.7	0.023	15	12.2	0.025	15	10.7	0.022	11
Epon 828	10.7	0.058	15	10.7	0.058	13	10.7	0.058	13			
DER 732				1.2	0.0038	1.5	1.96	0.006	2.4	18.2	0.057	20
DMP 30	2.1			2.25			2.4			2.1		
Ratio-PS to Epoxy	1:1	1:2.6	1:1	1:1	1:2.7	1:1	1:1	1:2.6	1:1	1:1.7	1:2.6	1:1.7
p-NASA · NH_3	43.3		60	47.6		60	49.2		59	55.3		59
Ratio-Binder to Salt by Wt.	1:1.84			1:1.84			1:1.80			1:1.78		
Refrasil	5.5		7.6	6.05		7.6	6.25		7.6	7.0		7.5
Thermal Efficiency sec/mm	80			39			43			37		
Thermal Expansion (Rise Times Orig. Thickness)	60X			10X			6X			4X		
Coating Thickness mm	1.5			2.3			0.9			2.2		

TABLE 3. COATING FORMULATIONS CONTAINING VARIOUS POLYSULFIDES

	M-12			M-14			M-15			M-16		
	Study of LP-3/LP-31 Blends			Study of LP-3/LP-31 Blends			Study of LP-3/LP-12 Blends			Study of LP-3/LP-31 Blends		
Components and Formulation	gm	eq	Wt %	gm	eq	Wt %	gm	eq	Wt %	gm	eq	Wt %
LP-3	80	0.16	11	35.5	0.071	3.7	46.5	0.093	6.0	26.6	0.053	3.7
LP-12							70.0	0.035	9.0			
LP-31	27	0.0068	3.7	108	0.027	11				81.0	0.02	11.2
Epon 828	107	0.58	15	143	0.77	15	116	0.625	15	107	0.58	15
DMP 30	21			28			22.5			21		
Ratio-PS to Epoxy	1:1	1:3.5	1:1	1:1	1:7.9	1:1	1:1	1:4.9	1:1	1:1	1:7.9	1:1
p-NASA·NH_3	433		60	575		60	465		60	433		60
Ratio-Binder to Salt by Wt.	1:1.84			1:1.83			1:1.82			1:1.84		
Refrasil	55		7.6	74		7.7	59		7.6	55		7.6
Thermal Efficiency sec/mm	53			44			Not Tested Because of Poor Flexibility			39.9		
Thermal Expansion (Expansion-Multiple of Orig. Thickness)	14X			16X			—			15X		
Coating Thickness, mm	1.9			1.8			—			1.8		

TABLE 4. HARDNESS DATA ON EPOXY-POLYSULFIDE COPOLYMERS

Components	F-25 (a)		F-25 (b)		F-25 (c)		F-25 (d)		F-25 (e)		F-25 (f)		F-25 (g)		F-26 (a)		F-26 (b)		F-26 (c)		F-26 (d)		F-26 (e)		F-26 (f)		F-26 (g)	
	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq
Epon 828	10	0.54	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054	10	0.054
DMP-30	2		2		2		2		2		2		2		2		2		2		2		2		2		2	
Ratio-PS:Epoxy	1:1	1:2.7	1:1	1:2.7	1:1	1:2.7	1.5:1	1:1.8	2:1	1:1.4	2:1	1:1.4	1.5:1	1:1.8	1:1	1:2.7	1:1	1:2.2	1:1	1:1.1	2:1	1:1.4	2:1	1:1.1	2:1	1:5	2:1	1:2.4
LP-3	10	0.02	5	0.01	2.5	0.005	15	0.03	20	0.04	10	0.02	5	0.01													10	0.02
LP-12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	10	0.005	—	—	—	—	20	0.01	—	—
LP-31	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	10	0.0025	—	—	—	—	20	0.005			10	0.0025
LP-33	—	—	5	0.01	7.5	0.015					10	0.02	10	0.02	10	0.02			—	—	20	0.04	—	—			—	—
Hardness, Shore D	50		45		45		20		—		—		13		76		60		67		—		32		28		—	
Hardness, Shore A	—		—		—		62		10		10		62		—		—		—		0(1)		—		86		54	

(1) Tacky — even after overnight cure at 160°F.

ORIGINAL PAGE IS
OF POOR QUALITY

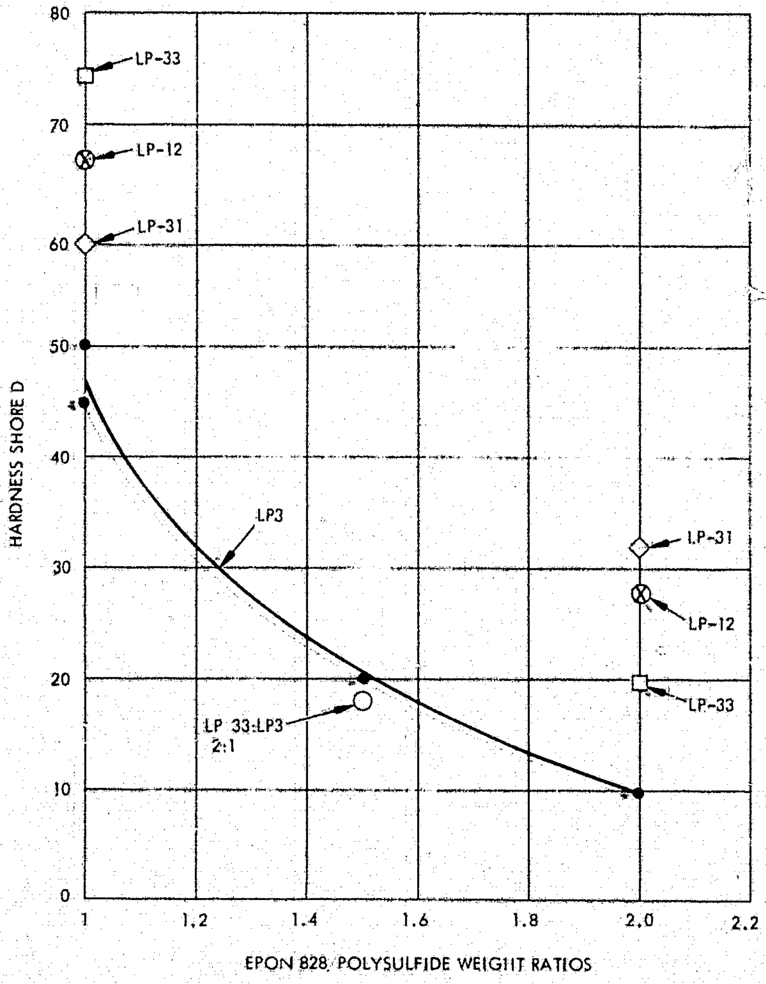


Figure 1. Hardness variations of Epon 828/polysulfide copolymers.

The results of the above tests indicated that an increase in the ratio of LP-3 to Epon 828 resulted in the most noticeable increase in flexibility. Accordingly, samples were prepared using an LP-3-to-epoxy weight ratio of 2.5:1 and 2:1, with Microquartz as the reinforcing fiber (Table 5).

A 2:1 ratio batch, formula M-17, in which the Microquartz had been mixed for 2 hours with the "Lightnin" mixer, was split into two parts. In order to determine the relative value of ball milling, one part was allowed to set overnight, and the other was ball-milled overnight (~16 hours). Each part was catalyzed and sprayed onto metal test plates. The ball-milled material provided a distinctly smoother sprayed coating than did the unmilled material, and the thermal efficiency was equivalent to the unmilled formulations as shown in Table 6. Ball milling thus appeared advantageous from the standpoint of promoting smoothness, and did not deleteriously affect the thermal efficiency.

Thermal expansion tests on the M-17 formulation and others containing a 2:1 weight ratio of polysulfide to epoxy showed very high expansion ratios — considerably above the 60X target value. Since excessive expansion can lead to dripping of the coating and blowoff, several formulations were made with lower polysulfide-epoxy ratios, 1.5:1 and 1.25:1 (by weight), as well as one with a 2.5:1 weight ratio. Thermal efficiency tests and thermal expansion tests indicated that these coatings would be very satisfactory. Thermal performance data for these compounds are shown in Table 7.

(4) Variations in Catalyst Content. In addition to changing the polysulfide-to-epoxy weight ratios, changes were also made in the catalyst content. These changes, which are described below, demonstrated that increased flexibility could be achieved by a reduction in catalyst content. The effect did not appear to be due to a mere change in cure rate, but rather due to a change in the relative rates of the epoxy-mercaptan addition reaction and the alkali catalyzed epoxy homopolymerization reaction. The ratio of epoxy resin to curing agent in the NASA-313 formula is approximately 5:1, or 20 phr.

TABLE 5. MODIFIED NASA-313 COATINGS, CONTAINING HIGHER POLYSULFIDE-TO-EPOXY RATIOS

Components and Other Parameters	M-19			M-20		
	Increased LP-3 to Epoxy Ratio			Increase in Microquartz %		
	gm	eq	wt %	gm	eq	wt %
LP-3	100	0.21	23	100	0.21	22
Epon 828	40	0.22	9.1	50	0.27	11
Weight Ratio: PS to Epoxy	2.5:1	1:105	-	2:1	1:1.3	-
p-NASA · NH_3	285	1.2	65	285	1.2	63
Weight Ratio: Binder to Salt	1:1.95	-	-	1:1.8	-	-
Microquartz	4.7	-	1.07	5.7	-	1.3
DMP-30	8	-	1.8	10	-	2.2
Coating Thickness	1.6 mm			1.5 mm		
660° F Thermal Expansion, Multiple of Original Thickness	60X			86X		
Thermal Efficiency sec/mm to 440° F (204° C) backface	57			63		
Flexibility — Bends over 1'' Diameter Rod	No			No		

LP-3 — Thiokol Chemical Co.
Epon 828 — Shell Chemical Co.
p-NASA·NH_3 — Nyanza Chemical Co.
Microquartz — Johns-Manville Corp.
DMP-30 — Rohms and Haas Corp.

TABLE 6. EFFECT OF BALL MILLING ON THE THERMAL EFFICIENCY OF 2:1 POLYSULFIDE-EPOXY MICROQUARTZ FILLED COATING

Formula M-17			
Formulation Details	gm	eq	Wt %
LP-3	214	0.43	27
Epon 828	107	0.58	14
DMP 30	21		
Ratios — LP3 to Epoxy	2:1	1:1.35	2:1
p-NASA · NH_3	433		55
Ratio-Binder to Salt by Wt.	1:1.26		
J-M Microquartz	7.5		1.0
Thermal Efficiency sec/mm	91, 72 Unmilled 88, 97 Milled		
Thermal Expansion	87X		
Coating Thickness mm	2.0		

Lee and Neville* state that DMP-30 is commonly used in amounts of from 50 to 15 phr when used as an epoxy homopolymerization catalyst, and the same amounts may be used to promote the polysulfide-epoxy addition polymerization. Thus, reduction in catalyst content theoretically could slow down the epoxy homopolymerization (which generates crosslinks) to a greater degree than it slows down the epoxy/S-H addition reaction (which yields only linear polymer); thus providing less crosslinked coatings with greater flexibility.

---

*"Handbook of Epoxy Resins," H. Lee and K. Neville, McGraw-Hill, 1967.

TABLE 7. EFFECT OF VARYING CATALYST CONTENT

Components and Formulation Details	M-22-1			M-22-2			M-22-3			M-23-1			M-23-2			M-23-3		
	gm	eq	wt %	gm	eq	wt %	gm	eq	wt %	gm	eq	wt %	gm	eq	wt %	gm	eq	wt %
LP-3	94	0.19	28	94	0.19	28	94	0.19	28	70.5	0.14	22	70.5	0.14	22	70.5	0.14	22
Epon 828	47	0.26	14	47	0.26	14	47	0.26	14	47	0.26	15	47	0.26	15	47		15
Weight Ratio: LP3 to Epoxy	2:1	1:1.4	—	2:1	1:1.4	—	2:1	1:1.4	—	1.5:1	1:1.9	—	1.5:1	1:1.9	—	1.5:1		—
p-NASA·NH_3 Salt	190	0.80	56	190	0.80	56	190	0.80	56	190	0.80	60	190	0.80	60	190	0.80	60
Weight Ratio: Binder to Salt	1:1.35	—	—	1:1.2	—	—	1:1.2	—	—	1:1.55			1:1.52			1:1.51		—
Microquartz	3.3	—	1.0	3.3	—	1.0	3.3	—	1.0	3.3	—	1.0	3.3	—	1.0	3.3	—	1.0
DMP-30	4.65	—	1.4	6.05	—	1.8	7.4	—	2.2	4.65		1.5	6.05	—	1.9	7.4		2.3
Coating Thickness	2.5 mm			1.6 mm			2.4 mm			2.4 mm			1.8 mm			2.0 mm		
350°C Thermal Expansion Multiple of Original Thickness	55X			86X			54X			85X			93X			54X		
Thermal Efficiency sec/mm to 400°F (204°C)	106						93			111			74			109		
Flexibility - Bends Over 1 inch Diameter Rod	yes			yes			yes			possibly			no			no		

LP-3 — Thiokol Chemical Co.
Epon 828 — Shell Chemical Co
p-NASA·NH_3 — Nyanza Chemical Co.
Microquartz — Johns Manville Corp.
DMP-30 — Rohms and Haas Corp.

ORIGINAL PAGE IS OF POOR QUALITY

A series of formulations was made using the same basic compounds, but catalyzed with varying amounts of DMP-30. The catalyst contents used were arbitrarily chosen as 50, 65, and 80 percent of the amount indicated in the NASA-313 specification. These various catalyst contents were used with formulations containing polysulfide-to-epoxy ratios of 2:1 and 1.5:1. The formulations and the thermal test results are also shown in Table 6. In general, it was felt that the 2:1 and possibly even the 1.5:1 polysulfide-to-epoxy weight ratios gave excessive thermal expansion. This was confirmed in a JP-4 fire test, when cylindrical steel tubes coated with a 2:1 weight ratio mixture exhibited what was considered excess intumescence, and dripped when suspended over the JP-4 fire.

(5) Initial JP-4 Fire Tests. With the development of the promising M-17 formula it was considered desirable to test the coating in an actual fire, on a simulated missile section. Thus a check could be made on the behavior of the coating under actual fire conditions, the adhesive bonded coating then could be compared to a sprayed coating, etc. The test procedure selected was chosen because it was inexpensive to use and because a rapid turn-around screening method was needed since new coating formulations were continuously being prepared.

An exploratory JP-4 fire test thus was made using two, 30.5 cm (12 inches) long, 12.7 cm (5 inch) diameter, 3.17 mm (0.125 inch) wall thickness, steel tubes. One tube was coated longitudinally over half its diameter with the M-17 coating (see Table 6) sprayed directly onto the sandblasted surface. The other half was coated with the pre-cured M-17 sheet material, which was bonded on with Haven Chemical Co. Epiphen 825A, a heat resistant epoxy adhesive. Selection of this adhesive was made strictly on the basis of experience and no comparative testing was performed prior to the selection. The second tube was also coated longitudinally, on half its diameter, with a sprayed M-17 coating, which after spraying and partial cure was smoothened down with a plastic film.

Both tubes were suspended over a 30.5 x 30.5 x 15.2 cm (12 x 12 x 6 inch) steel container into which approximately 2 inches of water and an inch of JP-4 were poured. After ignition, the tubes were adjusted so that the flames just touched the bottom of the tube.

In all cases good intumescence was observed. There was apparently no slippage of the bonded sample, as compared to the sprayed-on sample. The intumescence, in fact, may have been excessive, since it amounted to well over 3 inches in height, and a number of large foam sections dropped off from each sample, although intumescence continued from the remaining underlayer. Since this formulation contained only 1 percent Microquartz, as well as a 2:1 weight ratio of polysulfide to epoxy, these results served to indicate that additional formulation work was required, expecially to reduce dripping by increasing the Microquartz content.

e. Solventless Coatings

Because of the potential problem of shrinkage due to solvent entrapment, an investigation was made into the possibility of preparing a solventless coating composition. Such a formulation would have several advantages, other than the obvious one of elimination of solvent: (1) with such a material, plastic film can be placed on the top and bottom surface of a cast sheet, thus assuring that both surfaces will be very smooth; (2) operator judgment would be eliminated, since with a removable plastic film on top and bottom, there is no need to turn over cast sheet; (3) with a top plastic film the material can be rolled or molded to a precise dimension; and (4) the possibility exists of applying the material, in paste form, directly onto the steel tube, with additional savings in operator time and labor.

(1) Variation in Epoxy Viscosity. Initial tests were made to determine if solventless coatings could be produced which could be applied satisfactorily, since with no solvent the material might be too high in viscosity to be made into sheets. The first such coating was made using LP-3 and Epon 825, in order to take advantage of the lower viscosity of Epon 825 (4,000-6,000 cps) relative to the viscosity of Epon 828 (10,000-16,000 cps). The lower viscosity, it was felt, would make the material easier to sheet out. A coating was made, using mortar and pestle mixing. Qualitative tests, using a hot plate and an infrared lamp, indicated more than adequate thermal expansion. Using a roller and plastic films to form 1.6 mm (0.062 inch) thick coatings, it was found that the solventless material could be easily rolled to the desired shape and thickness.

The first solventless coating formulated used a weight ratio of epoxy resin to catalyst of approximately 5:1, which was the same ratio as that used in the NASA-313 formulation. Since previous formulations, M-22-1, -2, -3 and M-23-1, -2 and -3 (Table 7) indicated that a slight decrease in the catalyst content resulted in increased flexibility, it was decided to use this knowledge in formulating the solventless coatings. Formulations M-24-1, -2 and -3, using Epon 825 (and lower catalyst content, as compared to NASA-313), detailed in Table 8, show that the flexibility was indeed increased, as compared to formulations containing the higher amount of catalyst.

TABLE 8. COMPOSITION OF SOLVENTLESS COATING M24 WITH VARYING CATALYST CONCENTRATIONS*

	gm	eq	wt %	M24-
LP-3	21	0.04	22	
Epon 825	13.4	0.08	14	
Weight Ratio Polysulfide to Epoxy	1.56:1			
p-NASA Salt	57	0.24	61	
Weight Ratio of Salt to Binder	1.7:1	-	-	
Microquartz	1.5	-	1.6	
DMP-30	0.8	-	0.8	
Weight % DMP-30 based on Epon 825			6% 10% 15%	(-1) (-2) (-3)

*First Solventless Mixture Used Epon 825 for Lower Viscosity. Hand mixed with mortar and pestle. All samples were sufficiently flexible to bend over a 1" diameter rod.

With the initial success in making a workable coating using Epon 825, the same type of formulation was then made using Epon 828* and LP-3 in a 1:1.25 weight ratio. The formulation was somewhat harder to hand mix than those in which Epon 825 was used; however, using a small laboratory size three roll paint mill, very satisfactory paste-like mixtures were made. To make a small batch, approximately 180 gm, the following composition, shown in Table 9, and process sequence was followed.

The above ingredients were mixed for 5 to 10 minutes in a polyethylene beaker, using the "Lightnin" mixer. This resulted in a rough paste, which could then be rolled on the mill.

The paste was run through the mill four times to give a smooth homogeneous composition. Total time was approximately five minutes.

The material was removed from the mill and weighed. The amount of epoxy in it was calculated, and 12.5 percent (by weight) of DMP-30 was added to the mixture, and blended in, either with the three roll mill, or the "Lightnin" mixer.

The above operations, which take approximately 1/2 to 3/4 hour, result in a smooth paste, which contains no solvents. It can be rolled or molded to size with considerably better thickness control than can be achieved with the sprayed material. In addition, since no solvent is used, shrinkage is virtually eliminated resulting in better dimensional stability.

Table 10 shows other variations in the solventless system, i.e., lowered intumescent salt content to decrease intumescence and cost, and increased Microquartz content to minimize dripping, etc. Formulation M-25-S (Table 11) was an exception in that it was an Avco-NASA-313, formulation which was modified by adding Microquartz rather than Refrasil fibers (the substitution was made at Hughes). The optimum formulations based on Hughes tests, appeared to be M-29 and M-30. Samples of these two formulations, on steel plates were thermally tested by NASA/AMES. As a result of these tests M-30 was selected as the preferred formula since it was found to give the best char and best thermal efficiency. Results of these tests are shown in Table 12.

---

*Epon 828 is similar to 825 but has a higher viscosity and higher equivalent weight.

TABLE 9. COMPOSITION AND PERFORMANCE OF FIRST ROLL MILLED SOLVENTLESS COATING

Description	M-25		
	Solventless Mixture Roll Milled		
	gm	eq	wt %
LP-3	35.2	0.07	19.5
Epon 828	28.2	0.15	15
Weight Ratio Polysulfide to Epoxy	1.25:1		
p-NASA · NH_3	114	0.48	63
Weight Ratio of Salt to Binder	1.8:1	-	-
Microquartz	4.0	-	2.2
DMP-30	3.5	-	1.9
Weight % DMP-30 based on Epon 828	12%		
Coating Thickness, mm	2.51		
Thermal Efficiency Sec/mm to 400°F (204°C)	116		
Flexibility, Bends over 1 in. Dia Rod	Yes		

Based on the results of the tests it appeared that the M-30 coating formulation demonstrated the best balance of properties, namely flexibility, good charring characteristics and good thermal efficiency and thus was selected as the optimized coating for thermal/physical evaluation.

Shortly after initiating the study of milled, solventless coatings, some concern was expressed by the NASA Project Monitor regarding the effect of

Constituents and Performance Parameters	M-26			M-27			M-28			M-	
	Lowered p-NASA Salt Content			Lowered p-NASA Salt and Increased Microquartz			Slight Increase in Curing Agent			Increased Mi Maximum	
	gm	eq	wt %	gm	eq	wt %	gm	eq	wt %	gm	
LP-3	53	0.106	21	53	0.106	21	106	0.212	21	53	0
Epon 825											
Epon 828	42.5	0.23	16	42.5	0.23	17	85	0.45	17	42.5	0
Weight Ratio Polysulfide to Epoxy	1.25:1			1.25:1			1.25:1			1.25:1	
p-NASA Salt	153	0.65	59	140	0.59	56	280	1.17	56	140	0
Weight Ratio of Salt to Binder	1.6:1	—	—	1.5:1	—	—	1.5:1	—	—	1.5:1	—
Microquartz	6		2.3	10	—	4.0	16	—	3.2	18	—
DMP-30	5.3	—	2.0	5.3	—	2.1	12	—	2.4	6.4	
Weight % DMP-30 based on Epon 828	12%			12%			14%			15%	
Coating Thickness, mm	2.26			1.60			1.70			1.52	
350°C Thermal Expansion Multiple of Original Thickness	—			55X			31X			41X	
Thermal Eff Sec/mm to 400°F (204°C)	108			93 and 104							
Flex. - Bends over 1 in. Dia Rod	Yes			Yes			Yes			Yes (	

*Refrasil is used here.

FOLDOUT FRAME

TABLE 10. COMPOSITION AND PERFORMANCE OF IMPROVED SOLVENTLESS COATING FORMULATIONS

	M-29			M-30			M-31			Standard NASA 313		
	Increased Microquartz to Maximum Practical			Lowered Microquartz Slightly			Slight Increase in Microquartz			Included for Comparison Purposes		
t %	gm	eq	wt %	gm	eq	wt %	gm	eq	wt %	gm	eq	wt %
1	53	0.106	20	53	0.106	21	53	0.106	21	10.7	0.02	15
7	42.5	0.23	16	42.5	0.23	17	85	0.46	17	10.7	0.058	15
	1.25:1			1.25:1						1:1		
6	140	0.59	54	140	0.59	55	280	1.2	54	43.3		60
—	1.5:1	—	—	1.5:1	—					1.84:1		
3.2	18	—	6.9	12.4	—	4.9	30.5		6.0	5.5*		7.6
2.4	6.4		2.5	6.4		2.5	12.75		2.4	2.1		3.0
	15%			15%			15%					
	1.52			1.91			—					
	41X			64X			—					
	Yes (barely)			Yes (barely)								

TABLE 11. COMPOSITION OF A MICROQUARTZ MODIFIED "NASA-313" COATING

Formulation	M-25-S		
Description	Avco-NASA-313 Modified with Microquartz and Additional LP-3		
	gm	eq	wt %
LP-3	17.6	0.035	19
Epon 828	14.1	0.075	15
Weight Ratio Polysulfide to Epoxy	1.25:1		
p-NASA·NH_3	57	0.24	62
Weight Ratio of Salt to Binder	1.8:1	-	-
Microquartz	1.2	-	1.3
DMP-30	2.1	-	2.3
Weight % DMP-30 based on Epon 828	15%		
Flex. — Bends over 1 in. Dia Rod	Yes		

milling on the structure of the Microquartz fibers. Accordingly, microscopic studies were made to determine the effect. Samples were taken of material run through the mill once, twice and three times. Subsequent examination of the fibers, after burning off the organic matter, clearly indicated that the fiber lengths were considerably diminished. Thus, there was a distinct difference in fiber length in the unmilled and milled compositions; however, the fiber breakage appeared to occur almost entirely during the first milling cycle. In no case did the fibers become powdery; rather, after milling, they appeared to be very short. The milled fibers, also appeared to be smaller than fibers mixed into the coating, using the "Lightnin" mixer or solvent techniques.

PRECEDING PAGE BLANK NOT FILMED

TABLE 12. NASA THERMAL TESTS ON M-29 AND M-30 COATINGS

Formulation #	Average Expansion	Average Thermal Efficiency sec/mm	Coating Thickness	Comments
M-29	10.7X	118	57 mils	Excessive expansion, slight cracking, small fiber length
M-30	7.8X	163	59 mils	Uniform intumescence, good char stability, no cracking

(2) Process Technique Development for the Optimized Formulation

(a) Roller Preparation of Pre-cured, Curved Sheets. With the development of the M30 formulation, it was felt that the original concept of preparing sheets of coating between plastic films could not be done successfully. The simplest technique used to produce the 1.57 mm (62 mil) coating appeared to be by rolling a batch of material into a sheet, using a rolling pin or calendar type rollers. It was found that, when the coatings were rolled out, a film of polyethylene, Mylar or Teflon 0.05 to 0.127 mm (2-5 mils) thick placed on top of the mass inevitably became wrinkled and showed some distortion as rolling progressed. However, a sheet of 0.38 mm (15 mil) thick polypropylene, placed on top of the material, served to provide smooth, wrinklefree surfaces.

In order to roll a sheet to a definite thickness some type of spacer was required. One method tried involved the use of a [305 mm (12 in.) long x 50 mm (2 in.) diameter] Teflon rolling pin which was equipped with 1.78 mm (0.070 in.) cross-section rubber O rings at each end. Thus a batch of coating material placed in the center of a plate would then be rolled out to the O-ring thickness. Because of the compressibility of the rubber rings, these sheets were not completely uniform in thickness.

Subsequently a metal sheet [305 x 203 mm (12 x 8 in.)] was equipped with spacers [1.5 mm (0.062 in.)], on each of the long sides. Then, using a metal roller fairly satisfactory coatings could be made. The sheets, however, were still not perfectly uniform in thickness and cured sheets exhibited some internal voids, due to entrapped air. These voids could only be seen when the sheets were held in front of a bright light. Extrusion from an air-evacuated reservoir is expected to be quite effective in resolving this problem.

Since the various roller techniques did not appear to give completely satisfactory coatings, it was speculated that coatings molded at a relatively high pressure would provide virtually void-free sheets by compressing dissolved gasses to a negligible size. Consequently, press molding techniques were studied next.

(b) Press Molding. The first tests consisted of simply placing the mold in a press, and then compressing the material down in the open ended mold. A slight diminution in void size was noted; however, since the mold was open ended, apparently not enough pressure was developed to significantly reduce the number or size of the bubbles.

Another test consisted of placing the mold between the heated platens of the press. While this resulted in a semi-cured part fairly rapidly, the voids were even larger and more numerous, due undoubtedly to the fact that the air expanded on heating and not enough pressure was exerted to expel or compress the air in the bubbles.

Tests were then made using a positive pressure mold with a 16.5 x 11.5 cm (6-1/2 x 4-1/2 in.) cavity. At a pressure of 84 x 10^5 Pascals (1200 psi), good, void-free sheets were obtained when molded at 71°C (160°F). With the initial success of the subsized mold, a new mold was constructed which would give 305 x 203 mm (12 x 8 in.) sheets, 1.57 mm (62 mil) thick. Each of these sheets, molded flat, would then be curved prior to being fully cured. Tests were made with the new mold, and it was found that a ten minute open mold cure at 71°C (160°F), followed by 20 minutes at 70°C (160°F) under a load of 30 x 10^5 Pascals (400 psi) provided sheets which were flexible enough to be easily curved over the mandrel.

Unfortunately, a number of voids, ranging in size from microscopic to approximately 3.5 mm (1/8 in.) still appeared in the sheets, regardless of the pressure used, up to a maximum of 400 psi. (Higher pressures, with larger mold could not be attained in the press used.) It is estimated that these voids occupied approximately 5 percent of the sheet area. Thus, additional work is required to further perfect the process of sheet preparation and provide completely void-free materials. Nevertheless this method is the technique selected for specific formulations since it doesn't appear to effect the efficiency.

(3) Application of Solventless Coatings to Tubes

(a) Direct Application to Tubes. Tests were made to determine the feasibility of applying uncured coating directly to tubular surfaces, while simultaneously overlaying the coating with polypropylene film. Three methods were tried. (a) A curved squeegee type applicator was made so that the coating could be laid down longitudinally; however, with this procedure only fair success was achieved in applying a uniform coat. (b) Another attempt was made to apply the coating circumferentially. This was somewhat more successful. Two tubes were coated with 4 in. strips wrapped around them. One strip was installed using 1.52 mm (60 mil) thick, 12.5 mm (1/2 in.) wide, aluminum sizing rings around the tube. These acted as supports for the roller. (c) The third coating was installed using 1.78 mm (70 mil) cross-section rubber O-rings on the roller. In each case, it was difficult to produce a smooth overlap, and the necessity of rotating the tube and supporting it made this technique questionable for practical usage. These two coated tubes were used in a fire demonstration to NASA and Navy personnel in the course of a program review conducted at Hughes. There was no external evidence of voids, but since the coatings had not been examined with transmitted illumination it was not known whether they contained internal voids.

(b) Sheet Bonding Techniques. In the earliest studies, sheets were bonded to tubes, or flat substrates, using a heat-resistant epoxy adhesive. Subsequently, tests were made to determine if this adhesive could be eliminated by using uncured coating material (m-30) as the adhesive. It was found that the material functioned very well in this capacity and, where required, as a grouting material. Flat sheets were bonded at pressures of 1000 Pascals or more in a press, or by using vacuum bag pressure. Curved sheets were very easily bonded to tube sections. The latter technique (with the relatively low pressure) appears to give very satisfactory bonds, and could more satisfactorily be used for coating missiles than a press technique.

As a result of the initial fire tests run on tubes coated with the M-27 formulation, and before receiving the NASA/Ames test results, coatings M-29 and M-30 were prepared in order to check out these two formulations. In these formulations 5 and 7 percent Microquartz were used. Two tubes were coated completely with each material. Each tube was coated with three precured, curved sheets using Haven Chemical Co. Ephiphen 825A as the bonding agent. Since three longitudinal sheets were used per tube, each sample also had three longitudinal seams. In each case two seams were very narrow, 0.8 mm or less in width. The third seam on the M-29 sample (which contained 7 percent Microquartz) was approximately 5.0 mm (3/16 in.) wide, and the third seam on the M-30 sample (which contained 5.0 percent Microquartz) was approximately 1.6 mm (1/16 in.) wide. This resulted from the sheets being cut too small, due to operator inexperience with this technique. The tubes were being prepared for delivery to the NASA program monitor but application methods had not been perfected to the point that the preparation was free of all problems.

It was found that on assembly, the 5 mm seam became filled with adhesive, so it could not be grouted in with uncured coating material. It was decided to fire test the tubes at Hughes with the seam in this condition to determine if the intumesced coating would cover over the adhesive.

Both samples were tested in a JP-4 fire, and both showed good intumescence, with no tendency toward dripping and a harder char than ever before achieved. A slight amount of slippage was noted on the top surface of each sample, so that the bottom half of each tube, which was completely enveloped in flame, did show a thicker intumescent coat than did the top. The slippage and disproportionality between the top and bottom of the coatings were, however, considerably less than that shown in the M-27 formulation. The top portion of the tubes intumesced approximately 1.25 mm (1/2 in.), while the bottom intumesced approximately 38 to 50 mm (1-1/2 to 2 in.).

It was noted that the small, 0.8 mm (1/32 in.), seam appeared to fill in completely. The 1.6 mm (1/16 in.) seam, which was purposely on the bottom of the sample bearing the M-30 formula, did not coalesce completely, so its location was clearly indicated by a fine deep fissure-like crack in the intumesced coating. However, no free metal was exposed. The M-29 sample, which had the 5.0 mm (3/16 in.) seam on the bottom, was much worse. In this case the coating parted at the seam and pulled away from the tube, resulting in several inches of relatively bare metal on the bottom of the tube. Because the high temperature adhesive obviously did not intumesce and fill in the "wide" cracks, it was decided to use the uncured M-30 paste as the adhesive in subsequent work.

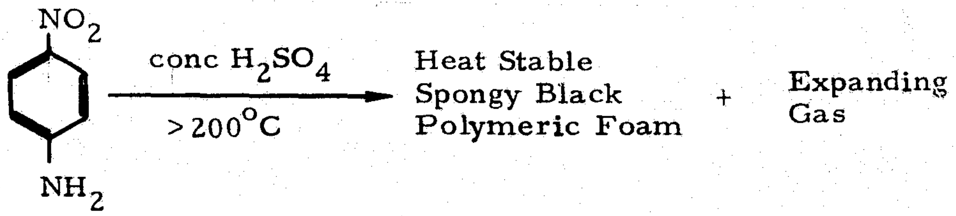
2. Phase II - New Intumescent Agents and Binders

a. Literature Review

Prior to initiating work on this part of the project, a literature search was conducted at libraries on the UCLA campus. The search was concentrated on obtaining information on intumescent compounds. The greatest portion of the information dealt with work reported by Cities Service Corporation, New York. References to patent literature were obtained and the patents examined. In general, the preferred chemical structures which were reported to intumesce and simultaneously char are sulfonamides, nitro aromatic amine sulfates, and nitro aromatic amine sulfonates. A more detailed discussion of these is presented below.

Intumescence is obtained via the foaming of a carbonizing melt which solidifies upon further heating. Three basic ingredients were reported to be necessary to provide successful intumescence. These are 1) a source of mineral acid catalyst, 2) a source of carbon, and 3) a blowing agent, i.e., a material which generates a large volume of gas upon heating. Numerous intumescent systems studied in the early work contained a source of phosphoric acid, a carbonizable polyol and a halogenated component. A great number of these formulations (which include, in addition to the necessary ingredients for intumescence, pigments, polymeric binders, bacteriostats, fungicides, colorants, flow and sag promotors or inhibitors, and other additives) are discussed in a review by H. L. Vandersall.[1] Literature through about 1969 is discussed in this review, which has 70 references.

A non-phosphorus approach to intumescence was initiated by NASA[2] in 1968. In this work, sulfate salts of nitro-substituted aromatic amines were shown to intumesce when heated to 180-260°C. This work was directed toward coatings for thermally sensitive substrates exposed to extremely hot fires. A typical reaction was illustrated as follows:



This process occurs with mono- or polycyclic substituted aromatics with available meta positions, e. g., p-nitroacetanilide, p- and o-nitroaniline and 5-nitroisatoic anhydride. The polymerization was stated to be specific for concentrated sulfuric acid. During polymerization, a fraction of the evolved gases are retained in the melt, forming a low-density carbonaceous foam.

The bisulfate salt of p-nitroaniline thus contains the three essential ingredients for intumescence in a single compound; however, because it is quite sensitive to water, it was of limited commercial value. In contrast, the ammonium salt of 4-nitroaniline-2-sulfonic acid affords intumescence without the use of highly acidic components.[3]

One difficulty encountered in the effective utilization of 4-nitroaniline-2-sulfonic acid ammonium salt and p-nitroaniline bisulfate as intumescent agents was the loss, through volatilization, of a portion of the p-nitroaniline.

Consequently, this was one of the problems for which a solution was sought in the current study.

One-component organic intumescent agents have been described extensively in the patents of Cities Service. Structures of numerous aryl-substituted sulfonamides which show intumescence are shown in these patents. Among these are polycyclic aromatic disulfonamides derived from naphthalene, anthracene, and phenanthrene; biphenyl- and terphenyl-disulfonamides,[4a] oxybis(benzenesulfonamide)monohydrate,[4b] methylenebis(benzenesulfonamide) and numerous other symmetrically substituted disulfonamides,[4c] p-aminobenzenesulfonamide,[4d] p-acetamidobenzenesulfonamide,[4d] arylsulfonamido-substituted pyridazines,[4e] pyrimidines,[4f] pyrazines,[4g] pyrazoles,[4h] triazines,[4i] oxadiazole[4j] and numerous derivatives of these compounds containing amino, alkylamino, arylamino, acylamino and halogen substituents. In addition, nitroaminobenzoic acid sulfates[4h] and certain nitro-substituted aminobenzoic acids, particularly 5-amino-2-nitrobenzoic acid[4l] are disclosed.

In a recent program conducted by the Dow Chemical Company under NASA contract NAS 2-4893, the synthesis of a variety of nitro-substituted aromatic amines was carried out. Thermogravimetric and differential thermal analysis data were obtained on these compounds and their sulfate salts in studying their intumescent behavior. With the compounds studied, the sulfate salts generally had lower temperature exotherms, and the magnitudes of these exotherms were greater than, or at least equal to, those observed with the free bases.

Typical compounds studied were the sulfuric acid salts of (1) 4-nitroaniline, (2) 3-methyl-4-nitroaniline, (3) 3,5-dimethyl-4-nitroaniline, (4) 2,6-dimethylaniline, (5) 2,3,5,6-tetramethyl-4-nitroaniline, (6) 2,4,6-trinitro-3, 5-dimethylaniline, (7) 2-nitro-3, 5-dimethylaniline, (8) 4-amino-5-nitro-2,1,3-benzothiadiazole, (9) 7-nitro-8-aminoquinoxaline, (10) 2-amino-4-nitropyrimidine, (11) N, N', N''-tris (4-nitrophenyl)-2,4,6-triamino-1,3,5-triazine, (12) 1-nitro-2-aminonaphthalene, (13) 2-amino-6-nitronaphthalene and (14) 2-amino-5-nitronaphthalene.

Two additional compounds studied were (15) 4-nitroaniline-2-sulfonic acid, and (16) N,N', N'' tris(2-sulfo-4-nitrophenyl)-2,4,6-triamino-1,3,5-triazine. These compounds were evaluated both as the free acids and as their ammonium salts rather than as sulfuric acid salts.

Thermal analyses performed by Dow gave the results shown in Table 13.

TABLE 13. THERMAL ANALYSIS OF POTENTIAL INTUMESCENT AGENTS STUDIED BY COLLINS

Compound No.*	Free Amine Exotherm, °C (DTA)	Degradation Temperature of H_2SO_4 Salt, °C (TGA)	Intumescent Temperature of H_2SO_4 Salt, °C (DTA)
1	360 (VS)	250-300	240-260 (VL)
2	335-360 (S)	225-300	225-250 (VL)
3	280-320 (M)	150-300	200-220 (VL)
4	325-360 (VS)		
5	300-340 (M)	175-225	165-200 (M)
6	285-325 (L)	175-225	150-205 (L)
7		125-250	175-225 (M)
8	none	100-400	100-125 (VL)
9	none	200-350	225-250 (L)
10	315-330 (S)	200-275	225-230
11	375-425 (VS)	125-300	200-275
12	250-325 (S)	125-350	135-145 (M)
13		80-350	130-175 (VL)
14			
15	300-320 (L)		
16	300-305 (VL)		

*See names designated by number on page 36.

b. Synthesis of Intumescent Compounds

Synthesis efforts were concentrated on the preparation of compounds which had the potential of serving as intumescent agents. Using the information obtained in the literature search, a number of candidate materials were selected for study, and were purchased or synthesized for evaluation.

General principles identified in the literature search as being important were followed: i.e., the materials selected for investigation as possible intumescent agents had sulfonic acid functional groups in the molecule to act in part as a polymerization catalyst and in part as a source of SO_2, there was an aromatic structure to furnish a high percentage of carbon in the char, and the material, on decomposition, evolved copious quantities of gas (SO_2) to act as a blowing agent and flame-quenching agent.

Compounds which met the above requirements could logically be substituted naphthalenes in which one of the substituents would be a sulfonic acid group and the other substituents would be amino groups and nitro groups to provide for polymerization and charring. Such compounds, in general, are similar to the 4-nitroaniline-2-sulfonic acid ammonium salt (p NASA salt) used in NASA-313, except that the naphthalene nucleus was expected to provide lower exotherms and higher char yields during decomposition.

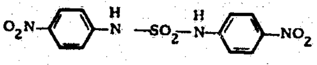
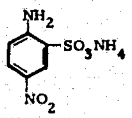
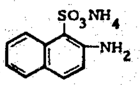
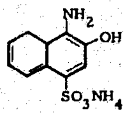
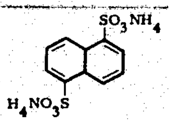
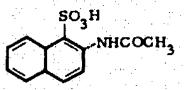
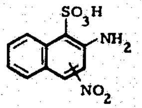
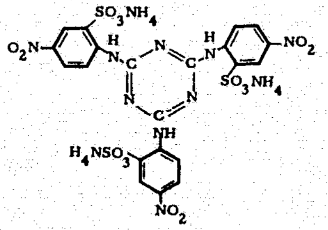
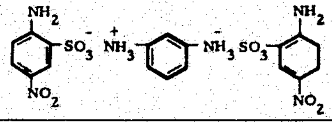
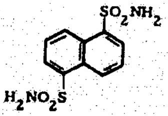
Ten candidate intumescent agents were procured and/or synthesized and their molecular structures are shown in Table 14. This table also summarizes the intumescent behavior.

The screening technique used for ascertaining the extent of intumescence consisted of heating a small quantity of the compound in an aluminum cup on a hot plate, while at the same time heating it from above with an ordinary 110 volt infrared lamp. With this test, N, N'-bis(4-nitrophenyl) sulfamide compound showed a rapid, highly vigorous intumescence. The p-NASA salt intumesced almost as vigorously. Both of these materials were used as standards against which other potential intumescent agents were compared.

Initial screening tests indicated that the four intumescent agents as well as the salt used in NASA-313 (intumescent agent No. 2) which warranted more extensive study were the following:

Intumescent agent 1.	N, N'-bis (4-nitrophenyl) sulfamide (Burdick and Jackson Laboratories).
Intumescent agent 10.	N, N', N''-tris (2-sulfo-4-nitrophenyl)-2, 4, 6-triamino-1, 3, 5-triazine triammonium salt.
Intumescent agent 11.	m-phenylenediamine salt of 4-nitroaniline-2-sulfonic acid.

TABLE 14. INTUMESCENT AGENTS INVESTIGATED ON THIS CONTRACT

Intumescent Agent No.	Report Page Ref.	Reference No.	Material	Structure	Remarks	Lab Book Page No.
1	40	IA-1	N-N'-bis(4-nitrophenyl)-sulfamide. (As received from Burdick & Jackson Lab:)		Intumesces well Burdick & Jackson Lot 0922, as received	T2627-77
2	Various	IA-2	4-nitroaniline-2-sulfonic acid ammonium salt. (p-NASA)		p-NASA salt from Ames 5/23/4. Good intumescence	
3	63	IA-3	Recrystalized IA-1 (isopropyl alcohol-water)	Same as IA-1	Hydrolyzed when recrystallized too slowly. No intumescence	
4	63	IA-4	2-amino-1-naphthalene-sulfonic acid, ammonium salt		No intumescence	H1284-34
5	64	IA-5	1-amino-2-naphthol-4-sulfonic acid ammonium salt		No intumescence	H1284-35
6	66	IA-6	1,5-naphthalene disulfonic acid, diammonium salt		No intumescence	H1284-38
7	66-67	IA-9	N,N'-bis(4-nitrophenyl)-sulfamide	Same as IA-1	Recrystallized from 2-propanol - water and NaOH. Very good intumescence	H1284-41
8	67-68	IA-10	2-acetamido-1-naphthalene-sulfonic acid		Decomposes and vaporized w/o discoloration at 253-275°C	H1284-40
9	66-67	IA-11	2-amino-3-nitro 1-naphthalenesulfonic acid		MP approx. 180°C with slight intumescence at MP	H1284-43
10	44 and 67	IA-12	N,N',N''-tris(2-sulfo 4-nitrophenyl)-2,4,6-triamino-1,3,5-triazine triammonium salt		Intumesces very well. TGA similar to IA-2. 325 C exotherm	H1284-49
11	46 and 68	IA-13	m-phenylenediamine salt of 4-nitroaniline-2-sulfonic acid		Good intumescence	
12	68	IA-14	1,5-naphthalene disulfonamide		Spot test on small sample appeared to intumescenced well.*	

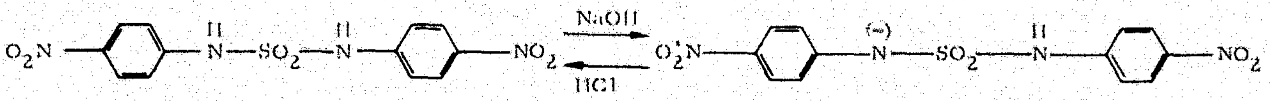
---

*Naphthalenesulfonic acid was ordered to allow more compound to be made, but due to a 6 month delivery from vendor additional material could not be made or tested.

Intumescent agent 12.	1, 5-naphthalenedisulfonamide.
Intumescent agent 2.	4-nitroaniline-2-sulfonic acid ammonium salt (p NASA salt).

Two additional compounds, originally considered for study – namely, the ditosylate of benzoquinone dioxime and the tosylate of benzoquinone monoxime – were deleted from further consideration, at the suggestion of the NASA Project Monitor, after one of the intermediates (intumescent agent No. 12) had been synthesized, namely, quinonemonoxime (tautomer of 4-nitrosophenol).

Intumescent Agent No. 1: N, N'-Bis(4-nitrophenyl) sulfamide. A mass spectrographic analysis of a sample of N, N'-bis(4-nitrophenyl) sulfamide (Burdick and Jackson Laboratories) (IA-1), showed that a small amount of p-nitroaniline was evolved at temperatures well below the intumescent temperature. This was recognized as an undesirable impurity; consequently, it was decided to recrystallize the sulfamide to obtain a purer product and hopefully to provide better intumescent properties. Two methods of recrystallization were used. One consisted of recrystallizing a quantity of the agent from an isopropyl alcohol-water mixture containing a small amount of carbon black. The yield with this technique was 84 percent, although the first time it was tried, excessive boiling hydrolyzed the compound extensively, probably because the hydrolysis is autocatalytic once it is started. The second technique consisted of a chemical method of separation, since it was found that the pure salt was soluble in 5 percent NaOH solution, whereas the nitroaniline was not. Thus, the N, N'-bis(4-nitrophenyl) sulfamide could be dissolved in aqueous alkali (5 percent, exp. H1284-48) and subsequently reprecipitated from solution by acidification with dilute aqueous HCl. Upon redissolving the precipated material in an ethanol-water mixture, and cooling overnight in a refrigerator, a 28 percent yield of N, N'-bis(4-nitrophenyl) sulfamide crystals having a melting point of 177°C was obtained. The purification proceeds through the following route.



To evaluate this intumescent agent, a standard NASA-313 type composition was prepared with the p-NASA salt replaced by the purified N, N'-bis-(4-nitrophenyl) sulfamide (IA-1). The coating composition was as follows:

Component	Weight (g)	Equiv.	Percent by Weight
LP-3	10.7	0.022	12
Epon 828	10.7	0.058	12
DMP-30	21.0		23
N, N'-bis (4-nitrophenyl)-sulfamide	43.3		48
Refrasil	5.5		6

Coated steel substrates (3" x 3") then were prepared and thermal efficiency measurements were made at a heat flux of 10 BTU/ft^2/sec. The thermal efficiency of 1.50 mm (60 mil) coatings averaged 81 sec/mm, and this was considered quite acceptable. Subsequently, the coatings were subjected to a humidity test by exposing them to 95-100 percent R. H. at 49° C (120° F). After 12-15 days, the thermal efficiency had dropped to 30 sec/mm and the thermal expansion ratio had dropped to 10X. The markedly reduced performance was not surprising in light of the fact that hydrolysis was noted in the course of the recrystallization studies. Hydrolytic instability of this intumescent agent thus appears to be a problem. As a consequence, further efforts to produce N, N'-bis(4-nitrophenyl) sulfamide based coatings were not pursued further at Hughes. This decision was concurred in by the NASA Project Monitor. The hydrolysis is assumed to be autocatalytic since sulfuric acid formed by hydrolysis would progressively reduce the pH as a function of time and the hydrolysis would be expected to be pH dependent.

Results of thermogravimetric (TGA) and the thermodifferential (DTA) analyses on samples of the sulfamide obtained by various purification procedures are presented in the appendix. Results of a DTA analysis and TGA analysis on the pure compound are shown in Figure 2 and 3 respectively. In the former, it is seen that the intumescent exotherm reaches a <u>maximum</u> of 200° C, whereas, the latter indicates that the onset of degradation is about 100° C., but that the extrapolated degradation temperature is about 220° C.

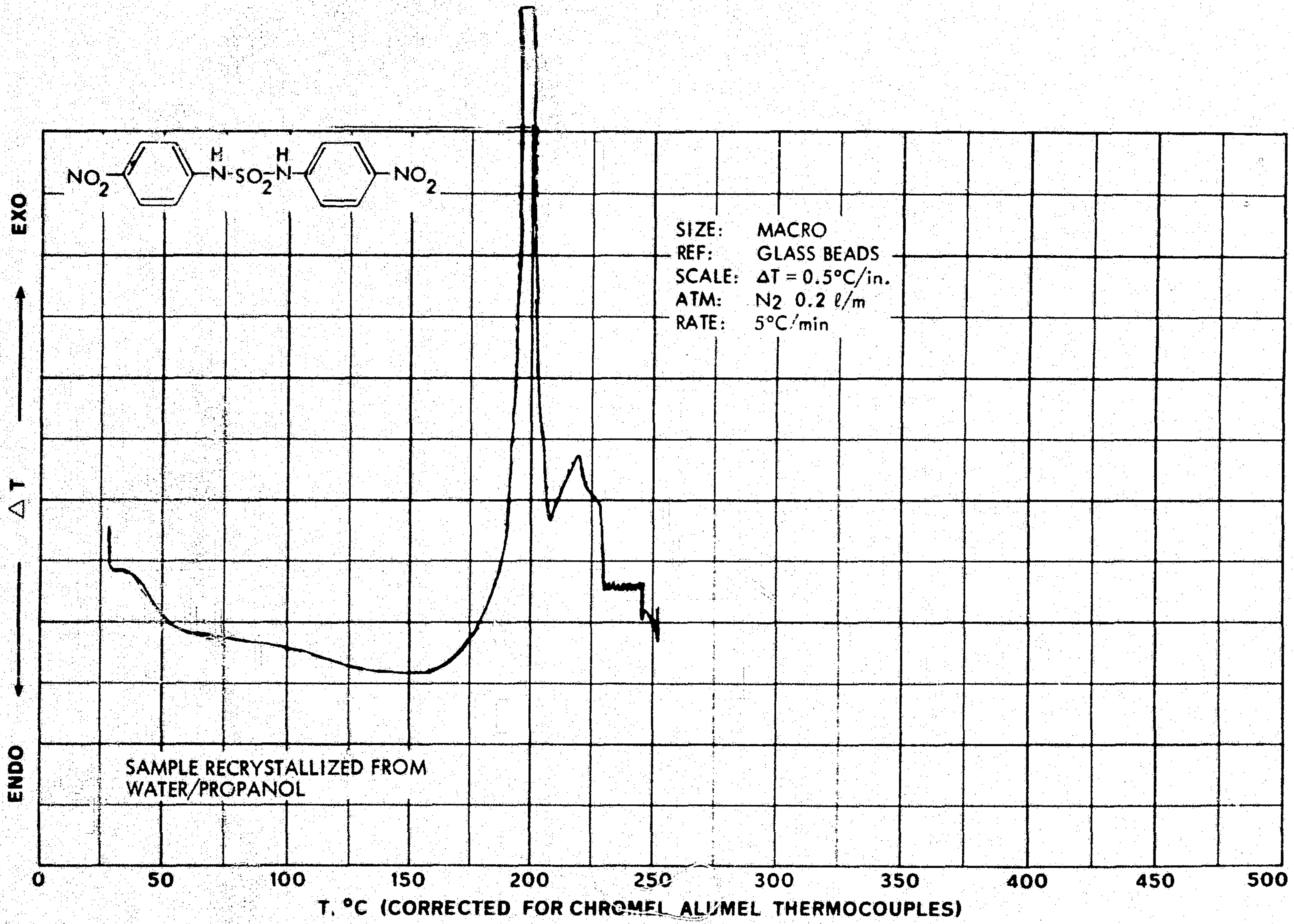


Figure 2. Differential thermal analysis of N, N'-bis(4-nitrophenyl)sulfamide (IA-1)

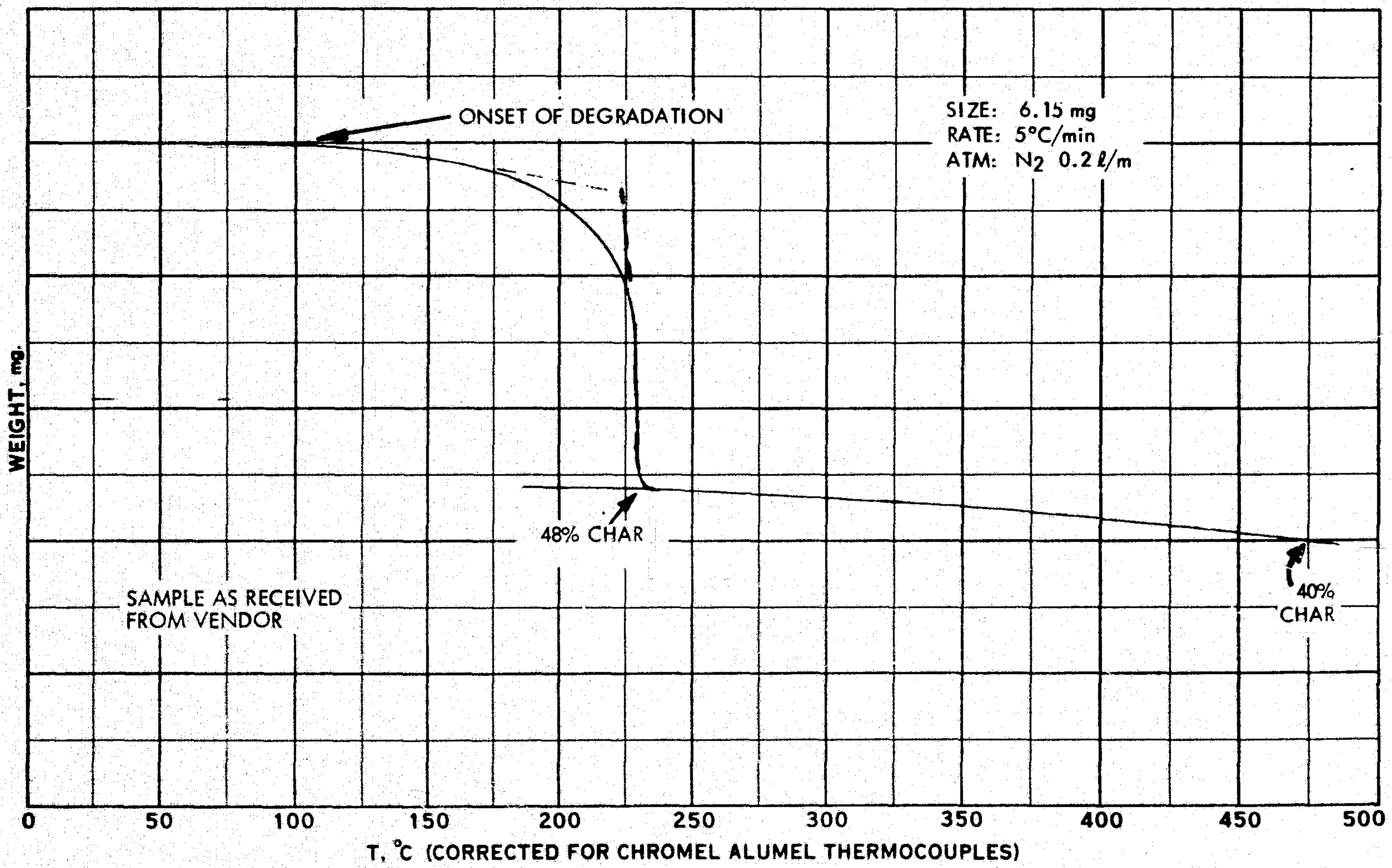
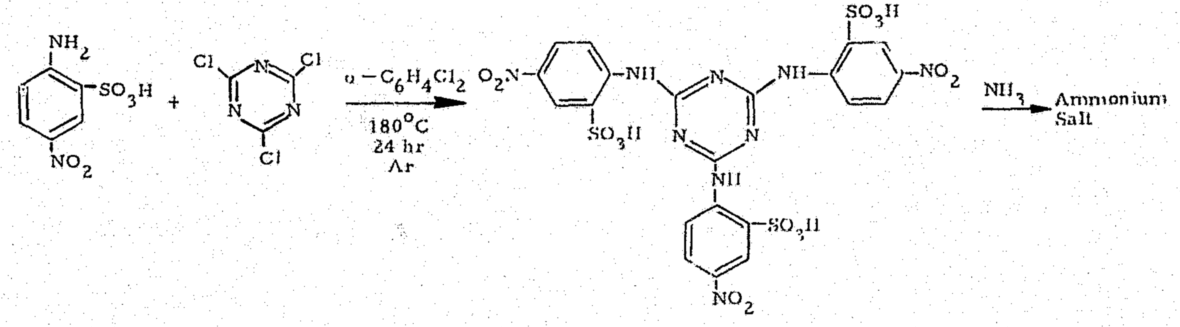


Figure 3. Thermogravimetric analysis of N, N'-bis(4-nitrophenyl)sulfamide (IA-1).

Intumescent Agent No. 10: N, N', N''-Tris(2-sulfo-4-nitrophenyl)-2, 4, 6-Triamino-1, 3, 5-triazine Triammonium Salt. Another intumescent agent investigated was N, N', N''-tris(2-sulfo-4-nitrophenyl, -2, 4, 6-triamino-1, 3, 5-triazine triammonium salt. This compound was synthesized by the process illustrated below.



Details of the experimental procedure are described in the appendix.

Differential thermal analysis results and thermogravimetric analysis results are shown in Figure 4 and 5. The DTA data shows an intumescent exotherm at 330° C whereas the TGA indicates a degradation temperature of about 350° C.

NASA-313 type coatings were prepared in which the p-NASA$\cdot NH_3$ salt was replaced on an equal weight basis, by the N, N', N''-tris(2-sulfo-4-nitrophenyl)-2, 4, 6-triamino-1, 3, 5-triazine triammonium salt. The coatings had an average thermal efficiency of 54 sec/mm (average of triplicate runs) with the best single value being 62 sec/mm. As with all other thermal efficiency tests, the heat flux was 10 BTU/ft^2/sec (11.35×10^4 watt/meter^2). The composition of these coatings is shown below. This efficiency was not as high as expected.

Components	Weight (g)	Eq.	Percent by Weight
LP-3	21.7	0.044	15
Epon 828	21.7	0.0117	15
Triazine salt	88		60
Refrasil	11.3		8
DMP-30	4.25		2.7

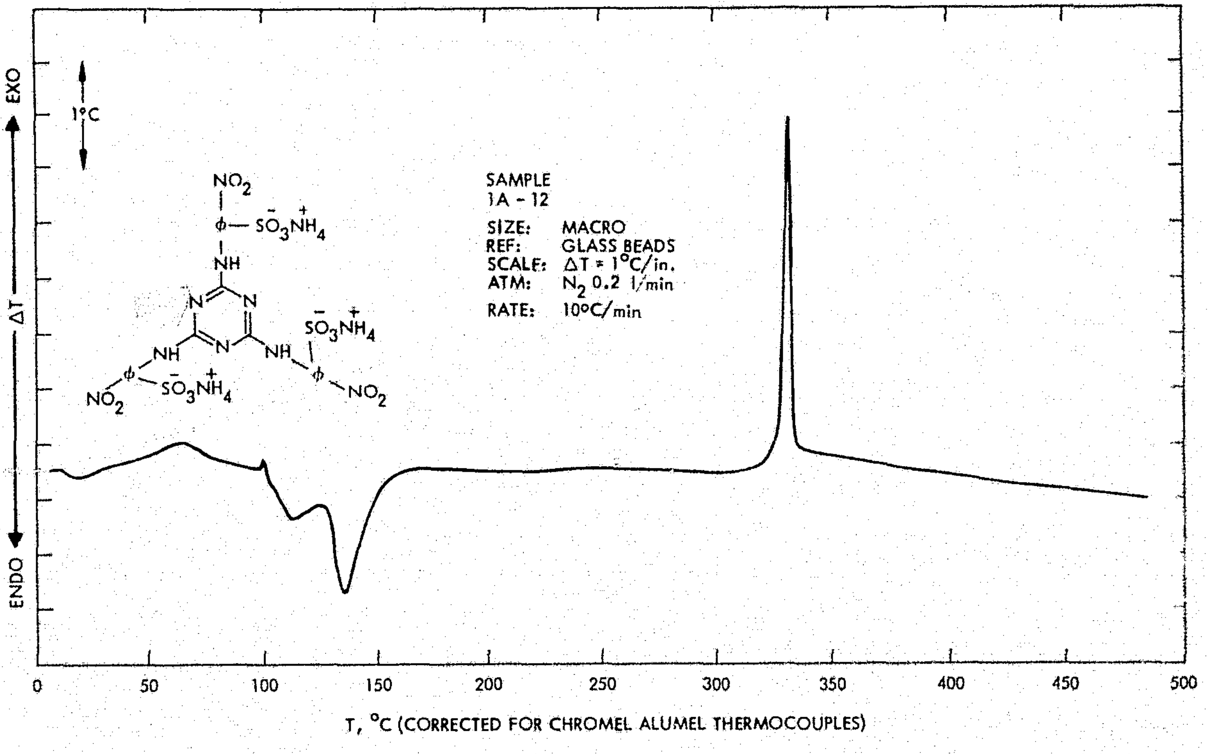


Figure 4. Differential thermal analysis of N, N', N''-tris(2-sulfo-4-nitrophenyl)-2, 4, 6-triamino-1, 3, 5-triazine triammonium salt.

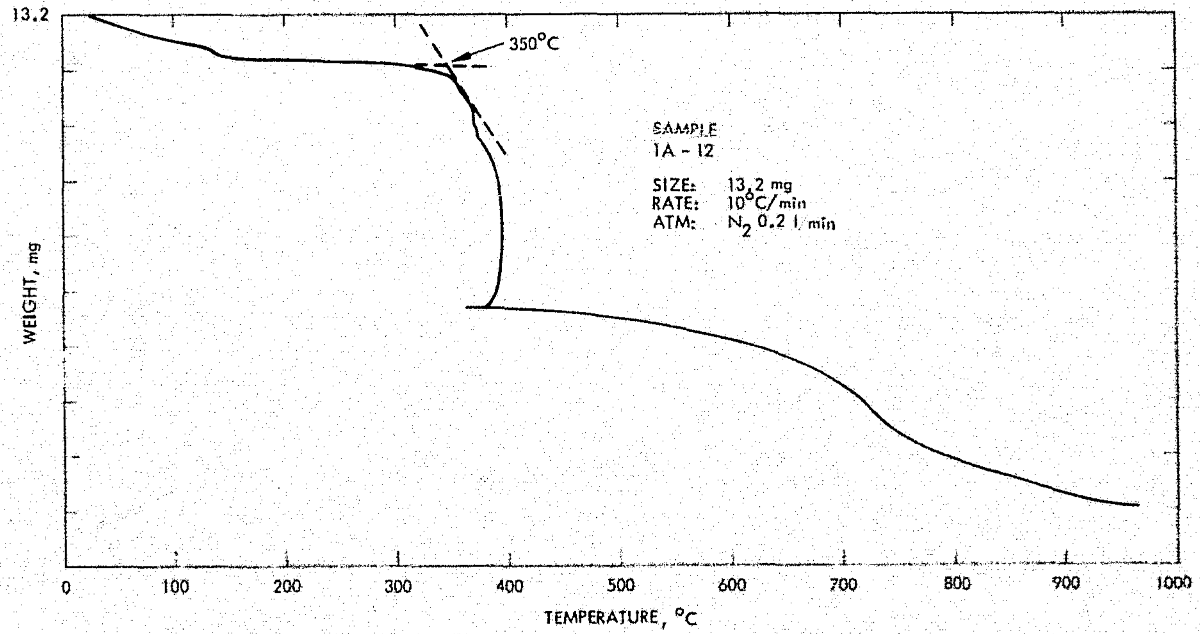
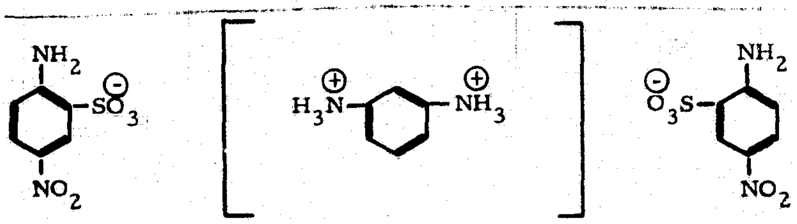


Figure 5. Thermogravimetric analysis of N, N', N''-tris(2-sulfo-4-nitrophenyl)-2, 4, 6-triamino-1, 3, 5-triazine triammonium salt.

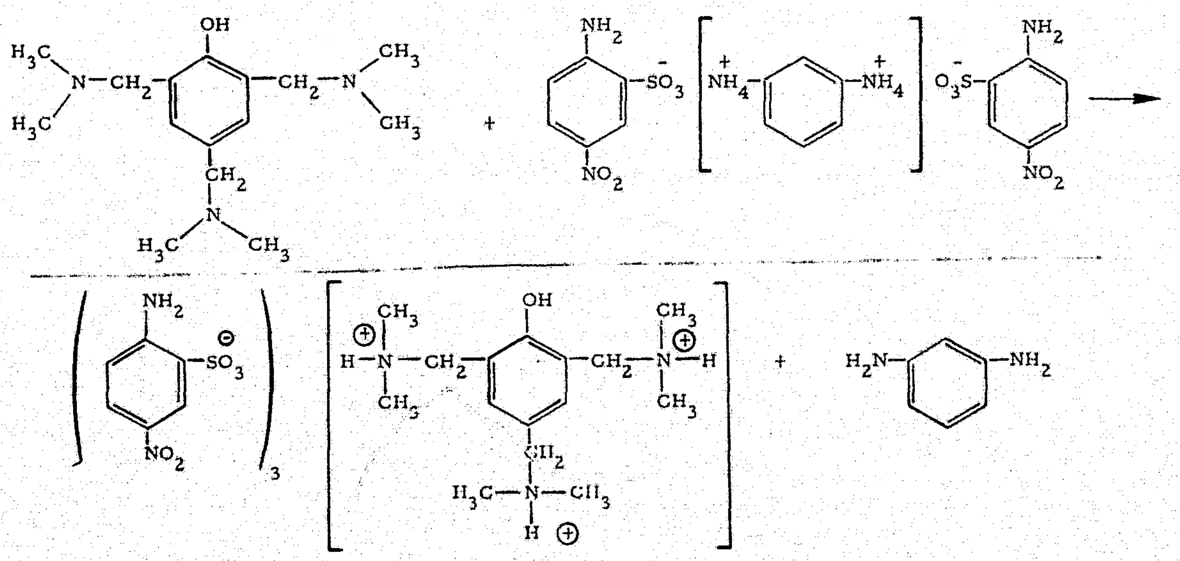
Intumescent Agent No. 11: m-Phenylenediamine Salt of 4-nitroaniline-2-sulfonic Acid. Another experimental intumescent agent examined was the m-phenylenediamine salt of p-nitroaniline-2-sulfonic acid. Its structure is shown below:



Experimental details of this preparation are described in the appendix.

Differential thermal analysis (Figure 6) showed the intumescent temperature of the salt to be 225° C to 235° C, and thermogravimetric analysis (Figure 7) indicated a degradation temperature of about 210-215° C, with a 300° C char yield of 36 percent.

Several attempts were made to formulate NASA-313 type coatings in which the p-NASA salt was replaced by the m-phenylenediamine salt. In each case it was noted that the addition of catalyst to the coating induced gelation. Subsequently, efforts were made to use diluted catalyst as well as greater coating dilution; nevertheless, relatively rapid gelation remained a problem. It is speculated that the greater basicity of the catalyst DMP-30 [tris(dimethylaminomethyl)phenol] relative to m-phenylenediamine allows it to replace the latter is illustrated below.



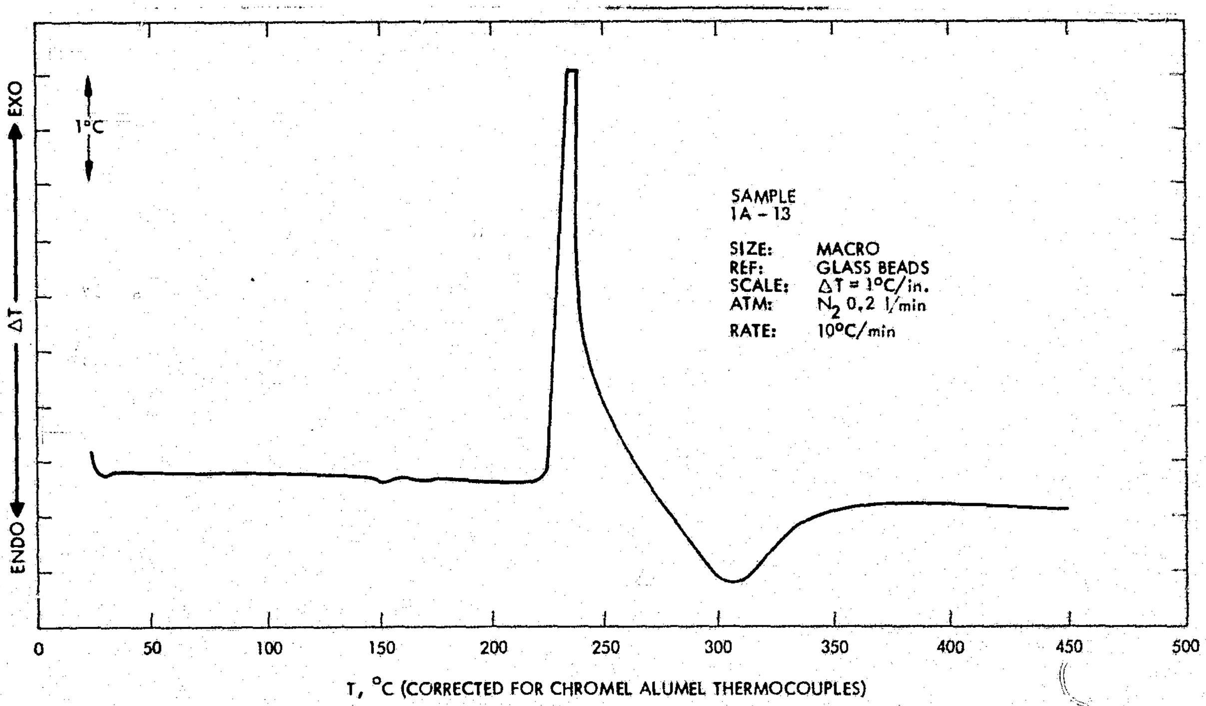


Figure 6. Differential thermal analysis of m-phenylenediamine double salt of 4-nitroaniline-2-sulfonic acid.

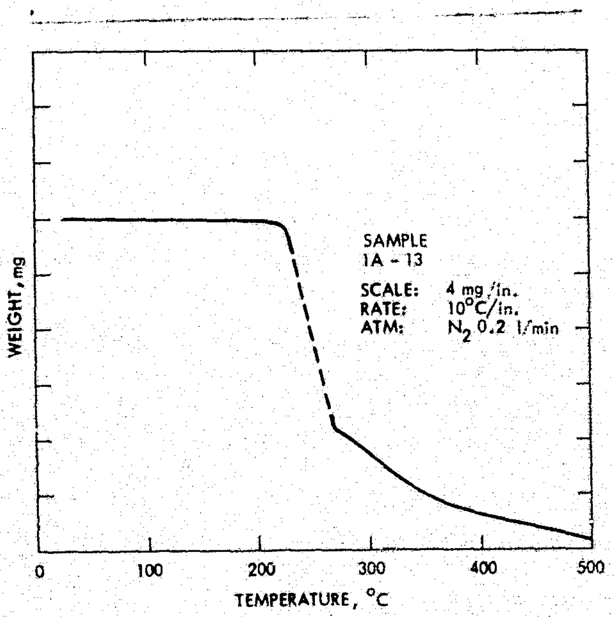


Figure 7. Thermogravimetric analysis of m-phenylenediamine double salt of 4-nitroaniline-2-sulfonic acid.

Because of the tendency to gel, sprayable coatings could not be obtained. Nevertheless, troweled coatings having a relatively rough finish were produced and tested for thermal efficiency. The compositions of two of these coatings, one made with Microquartz and the other with Refrasil, are shown in Table 15. Methyl ethyl ketone and toluene were blended with the individual components prior to coating preparation and the ratios were similar to those used in NASA-313.

Thermal performance tests showed that the Microquartz-filled formulation has a thermal efficiency of 38 sec/mm, whereas the Refrasil-filled formulation had a thermal efficiency of 77. In both cases these results are based on the time for the back face of specimens to reach a temperature of 204°C (400°F), using a heat flux of 10 BTU/ft^2/sec. Although the Refrasil formulations appeared to perform in a satisfactory manner, the tendency of the coatings to gel when the DMP-30 catalyst was added caused the elimination of the m-phenylenediamine p-NASA double salt from further study. It should be noted, however, that this salt may still be a good

TABLE 15. COMPOSITION OF m-PHENYLENEDIAMINE DOUBLE SALT COATINGS

Components	No. F27-1		No. F27-2	
	Weight (g)	Weight (%)	Weight (g)	Weight (%)
LP-3	49.5	16	49.5	15
m-phenylenediamine double salt	200	64	200	60
Microquartz	3.4	1.1		
Refrasil			25.5	7.6
Epon 828	49.5	16	49.5	15
DMP 30	10.0	3.2	10.0	3.0

candidate intumescent agent, if time and funds were available to permit research into a new catalyst/binder system. Work on this salt was terminated after concurrence by the NASA Project Monitor.

c. Coating Formulations

After synthesizing or otherwise procuring the new intumescent agents previously described, those which appeared promising on initial screening were compounded with polymeric binders to form coating compositions which could be tested for thermal efficiency and linear expansion.

Initial formulations were made using the new intumescent agents and the epoxy-polysulfide binder system used in the NASA-313 coating (Ref. NASA CR 114287), and in one case a polyurethane binder previously developed at Hughes under NASA Contract 2-5886. The NASA-313 epoxy-polysulfide formulation was to be used as a control. The first intumescent salts used were the p-NASA·NH_3 salt and the N, N'-bis(4-nitrophenyl)sulfamide. Small quantities were prepared using a mortar and pestle for grinding and a minimum of solvent, in order to develop techniques which would be adaptable to the production of many variations of a basic formulation.

Each formulation was given an initial screening test by simply heating it with an infrared lamp. To determine their ultimate potential, those formulations which appeared promising were applied to duplicate 7.6 x 7.6 x 0.152 cm (3" x 3" x 60 mils) abrasive-blasted steel plates. The plates, which contained an insulated disc in the center for a thermocouple, were similar to those used in the previous work. These coatings were applied by simple hand spreading, or trowelling, and were made to an approximate thickness of 1.5 mm. One coated metal sample then was used for the thermal efficiency test and the other sample used for a determination of the linear expansion ratio.

The formulations tested in this phase are listed in Table 16. These are listed by "F" numbers, and are listed roughly in the order in which they were prepared.

TABLE 16. COATING FORMULATIONS WITH NEW INTUMESCENT AGENTS

Formula No.			Candidate Intumescent Agent No.	Binder		grams	eq	Thermal Efficiency sec/mm
Book	Page	"F" No.		Type	Composition			
F2627	88	F-1	IA-1	Epoxy-polysulfide	LP-3 IA-1 Epon 828 DMP-30 MEK Toluene	2.82 11.4 2.82 0.56 as req. as req.	0.03 0.06	Sample too small to run. Screening test only
F2627	88	F-2	IA-3	Epoxy-polysulfide	Same as F-1 except for intumescent agent			Same as F-1
F2627	88	F-3	IA-2	Epoxy-polysulfide (NASA-313 formula)	Same as F-1 except for intumescent agent			Same as F-1
F2627	88	F-4	IA-9	Epoxy-polysulfide	Same as F-1 except for intumescent agent			Same as F-1
G1331	47	F-8	IA-2	Epoxy-polysulfide	LP-3 IA-2 Epon 828 DMP-30 MEK Toluene Refrasil	10.7 43.3 10.7 2.1 22.0 5.7 5.5	0.112 0.224	78
G1331	48	F-9[1]	IA-1	Epoxy-polysulfide	LP-3 IA-1 Epon 828 DMP-30 Toluene	24.7 100.0 24.7 4.8 ≈65.0		52
G1331	48	F-10[2]	IA-3	Epoxy-polysulfide	LP-3 IA-3 Epon 828 DMP-30 MEK Toluene	7.41 30.0 7.41 1.46 15.25 ≈4.00		51
G1331	48	F-11[3]	IA-3	Epoxy-polysulfide	LP-3 IA-3 Epon 828 DMP-30 MEK Toluene	4.94 20.00 4.94 0.975 10.16 ≈4.0		30 & 54 (duplicate samples)

[1] Very difficult to mix or disperse in toluene. MEK yields smoother mix, but product is thixotropic.

[2] Good dispersion in MEK. Dark brown gel when DMP was added to the LP-3-epoxy blend.

[3] Easy to disperse. Insufficient material for satisfactory application.

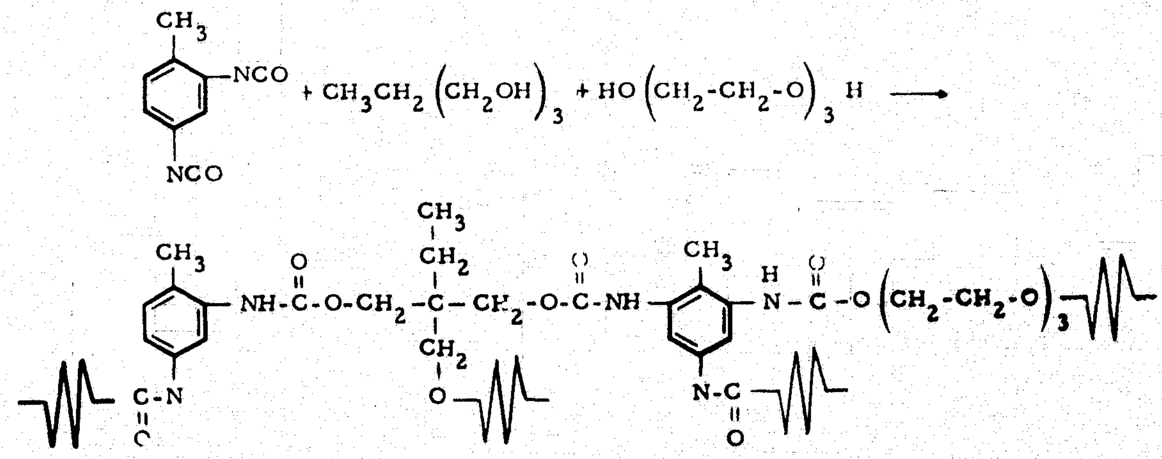
[4] Standard NASA-313 has a thermal efficiency of 75-80 sec/mm.

ORIGINAL PAGE IS
OF POOR QUALITY

Formulations F-8, F-9, F-10 and F-11 were prepared as sprayable coatings, F-8 being the standard NAS-313 coating, and the others having "new" intumescent salts substituted for the p-NASA$\cdot NH_3$ salt. Since the "new" formulations represented only the most promising intumescent compounds, they alone were tested for thermal efficiency, along with the control material. The poor results secured with the control then led to several more batches of control being made, as described in detail later. Since none of the "new" formulations appeared to give particularly high thermal efficiencies no further work was performed with them. Formulations F5-F7 were discarded and are not listed in Table 16.

d. Substitute Polymeric Binders

As mentioned previously a second approach to meeting the program objectives used in Phase I was one involving substitutions of the polymeric binders in the standard 313 system. In this approach it was decided to investigate at least one new binder system, but more particularly to evaluate a binder which in prior Hughes work looked very promising.[5] Consequently, one polymeric binder other than epoxy-polysulfide was investigated in the course of the program. This was a polyurethane derived from triethylene glycol, trimethylopropane, and 2, 4-tolylenediisocyanate. The polymerization is shown below



In the prior work, it was found that triethylene glycol:trimethylolpropane ratios of 1:1 to 1:2 were particularly good. Consequently, in this study the 1:1 molar ratio was used. In preparing the first few polyurethane coating formulations, the triethylene glycol (TEG) and trimethylolpropane (TMP) were mixed and then ground together with the dried intumescent salt. The tolylenediisocyante (TDI) and toluene then were added. It was noted that these formulations foamed somewhat during the cure, evidentally due to absorbed atmospheric moisture. To minimize this problem, it was decided to use urethane prepolymers, in which the TDI was partially reacted, rather than preparing the coatings directly from the monomers. Coated specimens produced with the first few formulations (made from monomers) all contained large amounts of voids and were not suitable for evaluation. Even with the two isocyanate prepolymers, and corresponding polyol mixtures, completely void free coatings were not obtained. Such coatings were, however, superior to those produced directly from the monomers.

Mixtures of the prepolymers with stoichiometric amounts of the corresponding polyol mixtures were prepared and used in preparing coatings with the compositions shown below.

Coating		2,4-Tolylenediisocyanate	Trimethylolpropane	Triethyleneglycol
I	Part A	174 g, 2 eq.	22.5 g, 0.5 eq.	37.5 g, 0.5 eq.
	Part B		22.5 g. 0.5 eq.	37.5 g, 0.5 eq.
II	Part A	174 g, 2 eq.	18.0 g, 0.4 eq.	45.0 g, 0.6 eq.
	Part B		18.0 g, 0.4 eq.	45.0 g, 0.6 eq.

The intumescent coating derived from II had the composition shown below.

p-NASA·NH_3	450 g
Triethylene glycol	90 g, 1.2 eq.
Trimethylolpropane	36 g, 0.8 eq.
TDI	174 g, 2.0 eq.
Toluene	as needed

Thermal tests conducted on this coating showed that it has a thermal efficiency of 45 sec/mm when tested with quartz lamps at the standard 10 BTU/ft^2/sec heat flux. This efficiency was not as high a value as expected considering the excellent results observed in our prior work.[5]

3. Phase III - Application of Optimized Coating to Hardware and Development of Material and Application Specifications

a. M-30 Coating Scale-up

In order to coat the missiles or simulated missiles, a large amount of material was required. The experience of making large batches, determination of storage properties, etc., was also required. A relatively large batch was prepared, at an outside facility, using pilot plant and/or production mixing and milling equipment.

Prior to the preparation of a large amount of coating material, tests were made to determine the shelf stability of the uncatalyzed M-30 paste. This was necessary, since the polysulfide and epoxy mixtures ordinarily can react in a relatively short time. Three samples (approximately 125 gm each) were prepared; one was kept at room temperature, another at -18°C (0°F), and the third in an oven at 49°C (120°F); 2 days later neither the room temperature sample nor the refrigerated sample showed noticeable changes in viscosity, nor any symptoms of filler settling. The 49°C (120°F) sample solidified in approximately 10 days. The room temperature sample showed satisfactory viscosity for 3 weeks, whereas the refrigerated sample was satisfactory for approximately 2-1/2 months.

Based on this shelf life study, an approximately 21 lb batch of material was prepared by Hughes personnel at the Furane Plastics Co.

The exact formulation (M-30) was:

	gm	Percent by Weight
LP-3	2082	21.4
Epon 828	1670	17.1
p-NASA · NH_3	5500	56.5
Microquartz	491	5.0

The DMP-30 catalyst (2.5%) was added at the time of use.

The materials were mixed initially in a 5 gallon stainless steel pot, using a dual speed Myers mixer. The mixer had an 8 in. propeller blade revolving at a relatively slow speed, and a high speed shearing disc simultaneously revolving. After the initial blending to work in the Microquartz, a thick, rough, putty-like mixture was obtained. The material then was given three passes though a three roll paint mill. During the first pass, a number of "dry" particles of Microquartz were seen. On the second pass, a very few particles were found, and on the third pass a smooth, creamy, thixotropic paste was obtained. The material was stored in a number of one quart jars to minimize contamination, container reaction and/or oxidation. The material stored in the refrigerator at approximately $5^{o}C$ ($40^{o}F$) showed signs of thickening at the end of 2-1/2 weeks. At the end of 3 weeks the material in the jars was too high in viscosity to be useful. Approximately one-half of the original 21 lb had already been molded into sheets when this occurred. Some of these sheets were curved for bonding to tubes, and some were kept flat for bonding to flat sheets.

b. Thermal/Physical Characterization of M-30 Formulation

The third phase of this program dealt with the comprehensive evaluation of the selected M-30 coating, and the fabrication of coated cylinders for delivery to the NASA project monitor. Both thermal and physical characterization was performed and the data was used in the preparation of a materials and process specification. The selection of the M-30 formulation was based upon the fact that this coating came closest to meeting the original goals set up at the onset of the program, i.e., it was smooth, it was cost effective, had good resiliency, was easy to apply, and met or exceeded the thermal expansion and thermal efficiency of the original formulation.

The application technique for the M-30 material, consisting of first molding and partially curing curved sheets, and then bonding them with uncured M-30, while not yet tested in production, appeared to be a process well suited for use on small diameter missiles.

After producing several small batches of M-30, molding a number of curved and flat sheets and bonding them to metal substrates, a material and application specification was prepared. This specification, Appendix II, was used as a guide in the preparation of a 21 lb batch of material which was subsequently used in the preparation of molded curved sheets.

The molded sheets, 305 x 203 x 1.5 mm (12 x 8 x 0.60 in.) were bonded to steel tubular sections using uncured M-30 as the adhesive.

Uncured M-30 was selected as the adhesive since qualitative tests on sheet samples bonded with it showed excellent adhesion. Its use as an adhesive precluded the necessity of procuring another material, and since it also intumesces, it acts the same as the M-30 sheets.

All of the semi-cured sheets were applied at vacuum bag pressure and finally cured 24-48 hours at room temperature followed by 16 hours at 72° C (160° F).

In addition to the production of the coated simulated missile sections, a number of 75 x 75 mm (3 x 3 in.) coated steel flat samples were prepared in accordance with the formulation and application requirements given in the referenced specification. These samples were all bonded at room temperature and at vacuum bag pressure. The samples were all aged approximately six weeks prior to initiation of the characterization tests. The results of the various evaluation tests are shown in Table 17.

TABLE 17. ENGINEERING EVALUATION TESTS

Test	Method	Results
Hardness	Shore durometer at room temperature.	98-99 (Shore A) 70-75 (Shore D)
Adhesion	≈ 1.9 mm (0.075 in. coating) bonded to 0.8 mm (0.032 in) Alodined aluminum sheet. Sample bent over a 25.4 mm (1 in) dia and 50.8 mm (2 in) dia mandrel	Samples cracked when bent over either mandrel
Impact Resistance	≈ 1.9 mm (0.075 in) coating (same as above) Gardner light duty impact tester 1G-115. Round nosed steel bar with 1/4 in. radiused end, 2 lb weight	22 inch pounds (US Navy data)
	Reverse impact	2 inch pounds
Abrasion Resistance	Taber Abraser (Model 174) CS-17 calibrase wheel, 1000 gm load	Wear index 0.66 mg/cycle
Humidity Resistance	Humidity cabinet 386 hours, 120°F, (49°C) 95% R.H.	Linear expansion 57X at 660°F
Lubricating Oil Resistance*	4 hours at 250°F (121°C)	Shore A hardness after test, 97-98
Temperature Shock	-60° to 160°F (-51° to 71°C)	Shore A 86 Shore D 35 (U.S. Navy data)
Intumescent Temperature	DTA	210°C (410°F)
Char Yield at 600°C (1112°F)	TGA in N_2	48 percent
Tensile strength		2219 psi (US Navy data)
Elongation		7 percent ultimate (US Navy data)

*95 percent di-2-ethylhexylsebacate (plexol 201-6-7505)
5 percent tricresyl phosphate.

IV. CONCLUSIONS

An intumescent coating designated M-30 was developed specifically for small diameter missiles. This coating is a modified version of NASA-313 with improved thermal efficiency and provides considerably smoother surfaces than the currently used NASA-313 formulation. Coatings can be produced as molded or extruded sheets, which are subsequently bonded to adherend surfaces. The M-30 coating formulation can also be used as the bonding agent to attach the coating sheets to substrates. In addition, it serves as a grout for filling cracks or crevices.

Formulation M-30, because of the solvent elimination and the use of 10 percent less p-NASA salt, has a lower materials cost per pound of finished coating than the currently used NASA-313. When the optimum production and application techniques have been fully developed, additional savings can be expected because operator application time should be lowered.

None of the potential intumescent agents studied were superior to the p-NASA · salt.

V. RECOMMENDATIONS

As a result of work performed on this program it was demonstrated that a new intumescent coating designated M-30 is useful for the fabrication of smooth flexible sheets suitable for bonding onto small diameter missiles. Coating formulation procedures and application techniques have been demonstrated but the processes have not been optimized.

As a next step the development of pilot plant techniques for the production of M-30 and application to full scale missile bodies is recommended.

The following are specific recommendations to implement such a pilot plant program:

a. Manufacturing scaleup procedures should be developed for producing M-30 reproducibly. Grinding, blending and milling procedures and equipment should be evaluated. Methods of adding Microquartz fibers must be examined so that fiber breakage is minimized. Long term shelf life tests should be run.

b. Techniques should be developed to produce large area sheets of Formulation M-30, which are as free as possible of internal and external voids. Extrusion of the coating through a slit orifice from an air-evacuated reservoir is the method which seems to be most worthy of evaluation.

c. Tests should be made to determine if small amounts of residual internal voids are detrimental. Since the charred coating is a foam, small internal voids may not have any effect on the final product.

d. Work also should be conducted on the development of techniques for applying the preformed sheets to missiles.

e. Various adhesives should be evaluated for bonding M-30 sheets to missile bodies. High resiliency adhesives may warrant special attention, especially a shock absorbing adhesive.

f. Additional work is recommended on the modification of M-30 to further reduce its production cost.

VI. REFERENCES

1. H.L. Vandersall, Journal of Fire and Flammability, 2, 97 (1971)
2. J.A. Parker, et al., SAMPE J., August/Sept. 1968, pp. 21-26
3. P.M. Sawko, et al, Journal of Paint Technology 44, pp. 51-55, August 1972
4. S.H. Roth, (a) U.S. Patent 3,759,741, (b) U.S. Patent 3,769,343, (c) U.S. Patent 3,748,173, (d) U.S. Patent 3,748,154, (e) U.S. Patent 3,769,083, (f) U.S. Patent 3,769,077, (g) U.S. Patent 3,769,073, (h) U.S. Patent 3,769,076, (i) U.S. Patent 3,769,082, (j) U.S. Patent 3,772,074, (k) U.S. Patent 3,703,409, (l) U.S. Patent 3,703,410
5. N. Bilow, et al, Study to Formulate Intumescent Coating Compositions, Final Report on NAS 2-5886, May 1972, p. V-12.

VII. APPENDIX 1.

DETAILED EXPERIMENTAL PROCEDURES FOR SYNTHESIS OF INTUMESCENT AGENTS

Purification of Intumescent Agent No. 1: N,N'-Bis 4-(nitrophenyl) sulfamide

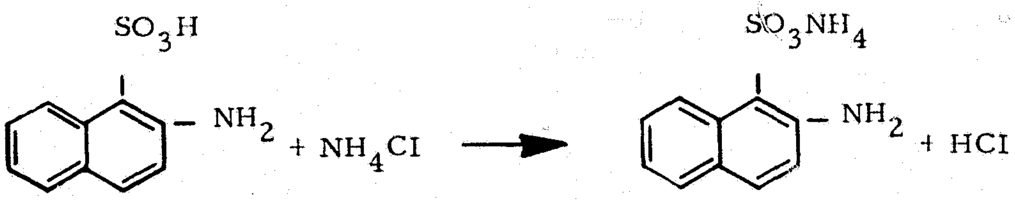
N,N'-Bis(4-nitrophenyl)sulfamide (200 g) was dissolved in aqueous sodium hydroxide solution (1200 ml, 5 percent). The bright red solution was immediately filtered, leaving a residue of p-nitroaniline behind (about 1 percent of total weight). The filtrate then was neutralized by the slow addition of hydrochloric acid. The yellow precipitate was filtered by vacuum and recrystallized from ethanol-water. The final yield of yellow crystals was 59 g (29 percent, m.p. 187-188°C).

A second batch of Burdick and Jackson N,N'-bis(4-nitrophenyl)sulfamide was treated as above with 5 percent aqueous sodium hydroxide, then slowly neutralized with aqueous HCl, and filtered. The product was washed with water and dried, without recrystallization. The yield was nearly quantitative.

Intumescent Agent No. 4: 2-Amino-1-naphthalene sulfonic acid ammonium salt

The ammonium salt of 2-amino-1-naphthalene sulfonic acid was prepared by the reaction of 2-amino-1-napthalene sulfonic acid with ammonium chloride as shown below.

PRECEDING PAGE BLANK NOT FILMED



Spot tests conducted on the compound indicated that it was not an effective intumescent agent and consequently further work on it was not performed.

The synthesis procedure was as follows. 2-Amino-1-napthalenesulfonic acid, 106 g (0. 5 mole), was slurried in distilled water (400 ml), then cooled to 0°C with an ice bath. Ammonium chloride, 27 g (0. 5 mole), in distilled water (300 ml) was added dropwise with stirring. The product precipitated and was removed by filtration with suction and washed with aqueous ammonium chloride, ethanol, and finally ether. The white solid, when dried, weighed 104 g (91. 2 percent yield). The crystals did not melt, but decomposed and sublimed between 290° and 330°C. No intumescence was observed.

Intumescent Agent No. 5: 1-Amino-2-naphthol-4-sulfonic acid ammonium salt

The ammonium salt of 1-amino-2-naphthol-4 sulfonic acid was prepared from the free acid by metatasis with ammonium chloride. The preparation is analogous to that used on the preparation of Agent No. 4. Initial screening tests indicated that the compound was not an effective intumescent agent and consequently work on it was terminated. Experimental details of the preparations are presented in the appendix. Differential thermal analysis results showed an endothermic degradation at 275°C but no intumescence.

The synthesis was performed as follows. 1-Amino-2-naphthol-4-sulfonic acid (27 g, 0. 11 mole) in 200 ml distilled water, was cooled to 0°C with an ice bath. Ammonium chloride (6 g, 0. 11 mole) in distilled water (50 ml) was added dropwise with stirring. The precipitate was collected by filtration on a Buchner funnel and washed consecutively with aqueous ammonium chloride, ethanol, and ether. After vacuum drying at 100°C, the pink solid weighed 24 g (84 percent yield).

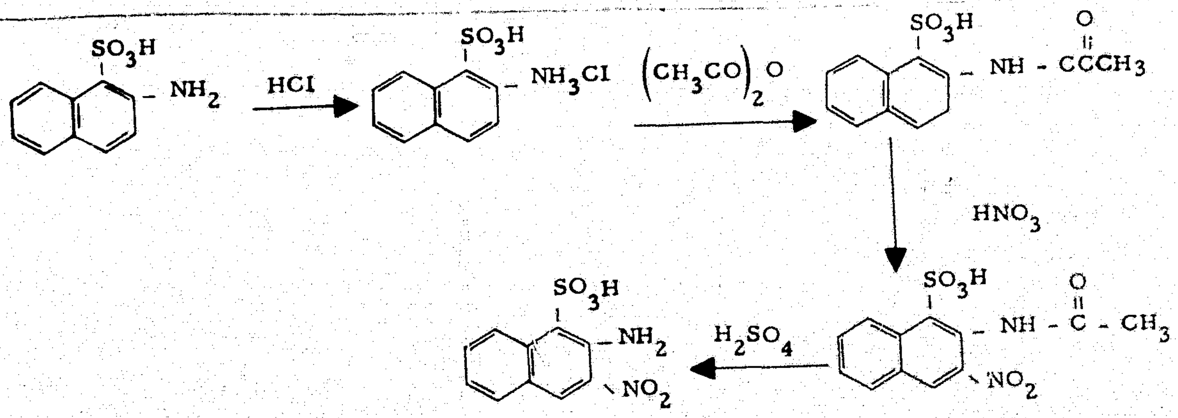
Intumescent Agent No. 6: 1-5-Naphthalenedisulfonic acid di ammonium salt

In an attempt to prepare 1, 5-naphthalenedisulfonamide by the reaction of the disodium salt of naphthalenedisulfonic acid with phosphorous pentachloride followed by treatment with ammonium hydroxide, a product was isolated which subsequently was found to be the di ammonium salt of naphthalenedisulfonic acid rather than the desired di imide. Screening tests were performed to determine if this product intumesced, but failing to do so, work on it was terminated. The salt sublimed without intumescing. Experimental details of the preparation are shown below.

1, 5-Naphthalenedisulfonic acid disodium salt dihydrate (104 g, 0. 28 mole) was heated at reflux in dry benzene to remove the water. The solid was removed by filtration and dried, then it was mixed with phosphorous pentachloride (117 g) and stirred. External heating was applied and the temperature rose to 106°C, the boiling point of phosphorous oxychloride. Dry benzene then was added to the cooled mixture to extract the organic materials. The extract was then stirred with aqueous ammonium hydroxide, producing a white solid. This was identified as the diammonium salt of 1, 5-naphthalenedisulfonic acid. The product weighed 21. 3 g (28 percent yield). Upon heating, it sublimed without intumescing.

Intumescent Agent No. 9: 2-amino-3-nitro-1-naphthalenesulfonic acid

3-Nitro-2-amino-1-naphthalenesulfonic acid was prepared by a four step process shown below



2-Amino-1-naphthalenesulfonic acid (100 g, 0.44 mole) and concentrated aqueous HCl (37 ml) were stirred in distilled water (1 ml) in a round-bottom flask, Then, acetic anhydride (53 ml) was added dropwise to the stirred mixture, after which a solution of sodium acetate (68 g) in distilled water (200 ml) was added all at once. An ice bath kept the the solution cold. After three hours of stirring, the solution was acidified with HCl and the crystals recovered by filtration. These were recrystallized from ethanol-water. The product (2-acetamido-1-naphthalenesulfonic acid) was a pink solid which sublimed at 263-275°C. It weighed 55.2 g and represented a 47 percent yield. It was dissolved in glacial acetic acid (45 ml) and mixed in a 1-liter beaker with concentrated sulfuric acid (85 ml). The mixture was cooled with an ice bath to 6°C. A mixture of concentrated nitric acid (12.3 ml), and concentrated sulfuric acid (8.0 ml) then was slowly added dropwise into the beaker. After stirring at room temperature for 2 hours, the dark-brown solution was poured into ice water. Since it would not filter, the solution was left to evaporate in air. The insoluble shiny purple solid which remained was triturated in hot benzene. When examined by infrared spectroscopy it appeared to be the desired product (3-nitro-2-acetamido-1-naphthalene-sulfonic acid). Hydrolysis of the acetamido group was carried out as follows: The product was heated at reflux with 70 percent sulfuric acid for several hours. Then the mixture was poured into ice water and filtered. The filtrate was evaporated and shown to contain mostly sodium sulfate. The solid product was the zwitterionic salt of the desired compound. It melted at 180°C and intumesced at this temperature. Spot tests conducted on the 3-nitro-2-amino-1-naphthalenesulfonic acid showed that it intumesced slightly when it melted at 180°C, but the intumescence was not good enough to warrent further evaluation.

Intumescent Agent No. 10: N,N'-N''-Tris(2-sulfo-4-nitrophenyl)-2,4,6,-triamino-1,3,5-triazine-triammonium salt. (H1284-49)

The free sulfonic acid derived from 4-nitroaniline-2-sulfonic acid ammonium salt was made in the following manner: The p-NASA·NH_3 salt (110 g) was heated in aqueous NaOH (300 ml, 6N) to drive off the ammonia. The solid was removed by filteration, and the sodium salt neutralized by the addition of sulfuric acid. The precipitated product was recovered by filtration, washed, and dried in vacuo. The total yeild was 66 g (65 percent).

Dried 4-nitroaniline-2-sulfonic acid (14 g), cyanuric chloride (4 g) and o-dichlorobenzene (210 ml) were heated at reflux (180°C) under argon for 24 hours. The mixture was cooled and the solid broken up, collected on a Buchner filter, and washed with hot acetone. Conversion of the free acid to the ammonium salt was achieved by stirring it in water with ammonium hydroxide. The isolated product weighed 7 grams. Differential thermal analysis showed the intumescent exotherm of the salt to be at 330°C. Two endotherms were also noted, the first presumably due to water. They were noted at 112°C and 135°C. Thermogravimetric analysis showed a 400°C char yield of 46 percent and a degradation temperature of 320 - 350°C. Both of the thermal analyses are illustrated in Figures 6 and 7.

Intumescent Agent No. 11: m-Phenylenediamine salt of 4-nitroaniline-2-sulfonic acid

This compound was prepared by adding dropwise a solution of m-phenylenediamine (108 g, 1.0 mole) in ethanol (1500 ml) to a solution of 4-nitroaniline-2-sulfonic acid (434 g, 2.0 mole) in boiling water (3l) and continuing the reflux for 4 hours. After cooling, the water and ethanol were removed with a rotary evaporator. The solid brown product was recrystallized from water after several activated charcoal treatments. After vacuum drying for 20 hours at 120°C, it weighed 433 g. The yield was 80 percent.

Intumescent Agent No. 12: 1,5-Naphthalenedisulfonamide

1,5-Naphthalenedisulfonamide was selected as a candidate intumescent agent after a screening test on an available sample had indicated it had good potential. However, to adequately evaluate it, naphthalenedisulfonic acid had to be ordered to prepare the diamide in a significant amount. Unfortunately, delivery from the supplier took over 6 months and it arrived when the project was virtually completed. Thus, no additional work was performed on this compound.

Synthesis of Binder Polymers: Isocyante prepolymers (H1475-03A)

A mixture of triethylene glycol (37.5 g, 0.5 eq), 1,1,1-trimethylolpropane (22.5 g, 0.5 eq) and toluene (100 ml) was heated at reflux until water evolution ceased, as evidenced by the evolved water in an azeotropic trap.

The mixture was cooled, and 2,4-tolylenediisocyanate (174 g, 2 eq) was added slowly while keeping the reaction temperature below 60°C. After stirring for 2-3 hours, the mixture was allowed to set overnight. The toluene was then removed under vacuum in a rotary evaporator while keeping the temperature below 60°C.

H1475-04A. A second copolymer was prepared in a similar manner, except that 18 g (0.4 eq) of trimethylolpropane and 45 g (0.6 eq) of triethylene glycol were used.

The "polyol" components prepared for use with each of these prepolymers was simply the anhydrous mixture of alcohols, in the same ratio as that used in the prepolymer.

VIII. APPENDIX 2

Specification No.

PRELIMINARY MATERIAL AND APPLICATION SPECIFICATION
For
M-30 THERMAL PROTECTION COATING

Chemical Research Projects Office
NASA-Ames Research Center
Moffett Field, California 94035

PRELIMINARY MATERIAL AND APPLICATION SPECIFICATION
For
M-30 THERMAL PROTECTION COATING

1.0 SCOPE

This specification covers the basic techniques of production and application as well as the minimum requirements for a molded thermal protection coating.

2.0 CLASSIFICATION

The thermal protection coating covered by this specification shall be classified as follows:

M-30

3.0 APPLICABLE DOCUMENTS

The following documents form a part of this specification:

Military

MIL-T-5624	Turbine Fuel, Aviation, Grades JP4 and JP5
MIL-A-8625	Anodic Coatings for Aluminum and Aluminum Alloys
MIL-C-5541	Chemicals, Films, and Chemical Fil Materials for Aluminum and Aluminum Alloys

Federal

FTMS No. 141	Paint, Varnish, Lacquer and Related Materials, Methods of Inspection, Sampling and Testing
TT-P-666B	Primer Coating, Zinc Yellow, for Aluminum and Magnesium Surfaces

TT-P-664b	Primer Coating, Synthetic, Rust-Inhibiting, Lacquer-Resisting
TT-P-86e	Type 3 Paint, Red Lead Base, Ready Mixed

4.0 REQUIREMENTS

4.1 Qualification

The thermal protection coating furnished under this specification shall be a product which has been tested and has passed the qualification tests specified herein.

4.2 Material

The thermal protection coating furnished under this specification shall conform to and shall be prepared using materials in accordance with the following formulation:

Material	Parts by Weight
Part A	
Polysulfide Liquid Polymer, LP-3 (Thiokol)	21.4
Epoxy Resin, Liquid. Shell Epon 828, or equiv.	17.1
Ammonium Salt of 4-nitroaniline-2 sulfonic acid (Nyanza).	56.5
Johns-Manville Microquartz, Code 108	5.0
Part B	
Tri (dimethylamino methyl) phenol. (Rohm and Haas DMP 30)	2.5

4.3 Properties

4.3.1 Physical Properties

4.3.1.1 Appearance. The appearance of the thermal protection coating shall be a yellow, hard, smooth (20 microinches maximum) integral sheet when examined as specified.

4.3.1.2 Tensile Strength. The tensile strength of the thermal protection coating shall be 2000 psi minimum when tested as specified.

4.3.1.3 Density. The density of the thermal protection coating shall be 1.50 ±0.05 g/cc when tested as specified.

4.3.1.4 Char Yield and Temperature of Intumescence. The char yield of the thermal protection coating at 1112°F shall be 46 ±3 percent, and the temperature of intumescence shall be 545° ±27°F, when tested as specified.

4.3.1.5 Abrasion Resistance. The abrasion resistance of the thermal protection coating shall not exceed a 700 milligram weight loss/1000 cycles on the Taber Abraser when tested as specified.

4.3.1.6 Flexibility. The flexibility of the thermal protection coating shall be 20 in-lb minimum when tested as specified.

4.3.1.7 Linear Expansion (Intumescence). The linear expansion of the thermal protection coating conditioned at 73.5° ±3.5°F and 50 ±5 percent R.H. for seven days shall be a minimum of 60 times the original coating thickness when tested as specified. The linear expansion of the thermal protection coating conditioned for seven days in a warm-humid atmosphere of 100° ±3.5°F and 90 ±2 percent R.H. shall be a minimum of sixty times the original coating thickness when tested as specified.

4.3.1.8 Thermal Efficiency. The thermal efficiency of the thermal protection coating shall be a minimum of 125 seconds/mm at 0.060 + 0.005 inches coating thickness to reach a backface temperature of 400°F when tested as specified.

5.0 DISPERSION EQUIPMENT

Machine Mixing. A propeller type mixer and a three roll paint mill or equivalent.

6.0 MIXING PROCEDURE

6.1 Fiber Preparation

Place Microquartz fibers in an oven for 24 hours. Remove fibers from the oven and allow to cool to ambient temperature.

6.2 Machine Mixing

Add the ingredients of para. 4.2 part A, in the order shown to the propeller driven mixer. Mix to a uniform thick paste. The Microquartz should be added in small quantities, and each quantity should be thoroughly absorbed before adding another quantity.

After mixing with the propeller mixer, transfer the paste to a three roll paint mill and mill three times or as required to obtain a smooth paste, with no trace of the white Microquartz fibers.

If the material is not to be used immediately it may be stored in glass or polyethylene containers (not tinned containers) at -40 ±5°F for up to 3 weeks. If it is to be used immediately then the requisite amount of part B shall be added to part A at this stage. The mixing may be done manually, or by a propeller mixer then another pass on the mill.

Note: The amount of part B to be added is 15 percent by weight of the calculated amount of epoxy in part A, after removal from the mill.

7.0 UNCURED COATING REQUIREMENTS

7.1 Qualifications

The wet coating furnished under this specification shall be a product which has been tested and has passed the qualification tests specified herein.

7.2 Part A – M-30 Thermal Protection Coating

7.2.1 Viscosity

The viscosity of Part A of the M-30 coating shall be _____ cps when tested as specified.

7.2.2 Weight Per Gallon

The weight per gallon of Part A of the M-30 thermal protection coating shall be 12.4 ±0.1 pounds/gallon when tested as specified.

7.2.3 Weight Percent Binder

Weight percent LP-3 polysulfide and Epon 828 epoxy resin extracted from Part A shall be 38.5 ±1 percent when tested as specified.

7.2.4 Weight Percent Solids

The combined weight percent ammonium-p-nitroaniline-o-sulfonate and Microquartz filtered from Part A shall be 61.5 ±3 percent when tested as specified.

7.2.5 Equivalent Weight

The equivalent weight of the sample from 7.2.4 shall be 235 ±12 based upon an adjustment for a theoretical value of 91.9 percent ammonium salt and 8.1 percent fibers when examined as specified.

7.2.6 Test for Intumescence

A sample from 7.2.4 shall intumesce when tested as specified.

7.3 Part B, M-30 Thermal Protection Coating

7.3.1 Index of Refraction

The index of refraction shall be 1.5188 ±0.0005 when tested as specified.

7.3.2 Density

The density shall be 0.964 ±0.002 at 22.4 ±0.2°C when tested as specified.

8.0 QUALITY ASSURANCE PROVISIONS

8.1 Responsibility for Inspection

Unless otherwise specified in the contract or the purchase order, the supplier is responsible for the performance of all the inspection requirements as specified herein. The supplier may utilize his own facility or any commercial laboratory acceptable to ARC. The processing activity, or its designated representative, reserves the right to perform any or all of the inspections set forth in the specification where such inspections are deemed necessary to ensure that supplies and services conform to the prescribed requirements.

8.2 Classification of Examinations and Tests

All of the examinations and testing of the thermal protection coating shall be classified as qualification tests. Qualification tests shall be performed on samples submitted for approval as qualified products and shall be performed on individual lots of products submitted for acceptance. The qualification tests are listed in Table 1, Page 75. A certified test report from the supplier shall accompany each product submitted for approval and each lot of thermal protection coating submitted for acceptance.

8.3 Sampling

The material preparation shall conform to the requirements of Paragraph 4.2 herein. A test report from the supplier shall accompany each sample to be tested, and shall show the composition number and the Test results for all requirements of this specification and shall refer specifically to the applicable paragraphs herein. All the thermal protection coating manufactured and formulated as one batch shall be considered a lot and shall be numbered as such for purposes of inspection.

8.3.1 Rejection and Retest

Failure of any lot to conform to all applicable requirements of this specification shall be cause for retest. Property or properties in question shall be retested on new specimens prepared from the same lot of thermal protection coating. If the results of test of the second sample fail to meet the specification requirements, the entire lot shall be rejected.

8.4 Part A, M-30 Thermal Protection Coating

8.4.1 Viscosity

Use a Model RVT Brookfield Viscometer with spindle at RPM or a Model Brookfield Viscometer with spindle at RPM and a temperature of

TABLE 1. WET COATING REQUIREMENTS

	Requirement	Test Method
Part A		
Viscosity	7.2.1	8.4.1
Weight Per Gallon	7.2.2	8.4.2
Weight Percent Binder	7.2.3	8.4.3
Weight Percent Solids	7.2.4	8.4.4
Equivalent Weight	7.2.5	8.4.5
Intumescence	7.2.6	8.4.6
Part B		
Viscosity Index of Refraction	7.3.1	8.5.1
Density	7.3.2	8.5.2

68°F. The result shall conform to Paragraph 7.2.1. However, viscosity measurements have been made on only a limited number of samples and acceptable ranges relative to application have yet to be determined. See report attached.

8.4.2 Weight Per Gallon

The test method shall be as described in Federal Test Methods Standard No. 141A, Method 4184.1. The result shall conform to Paragraph 7.2.2.

8.4.3 Weight Percent Binder

After careful stirring, weigh out a 100 gm sample of Part A and mix in approximately 100 ml toluene. Separate the slurry by suction filtration and wash the solids with 2 additional portions (100 ml) of toluene. Collect the filtrate and evaporate the solvent in a tared flask using a rotary evaporator with gentle heating. Calculate the residue as percent binder.
Theory 40 percent.

8.4.4 Weight Percent Solids

Dry the solids collected from 8.4.3 on a tared filter paper to constant weight at 167°F in a circulating oven. Theory 60 percent combined salt-Microquartz.

8.4.5 Equivalent Weight

Weigh out 3.0 gms solids from 8.4.4 and adjust to theoretical weight of ammonium salt (x 0.919). Adjusted weight is 2.75 gms. Suspend the material in 100 ml of 50 percent by volume aqueous methanol and titrate with 1.0 N•NaOH using a recording electrometric titrator. From the volume of the titrant to reach end point, calculate the equivalent weight. The result shall conform to Paragraph 7.2.5.

8.4.6 Linear Expansion (Intumescence)

Place a dry sample from 8.4.5 into an oven at 660°F for 1/2 hour. Material shall exhibit linear expansion.

8.5 Part B, M-30 Thermal Protection Coating

8.5.1 Index of Refraction

The index of refraction shall be determined at 22 ±0.5°C (72 ±1°F) and the result shall conform to Paragraph 7.3.1.

8.5.2 Density

The density shall be determined in accordance with Federal Test Methods Standard No. 141A, Method 4183.

9.0 APPLICATION PROCEDURE

9.1 Substrate Preparations

9.1.1 Cold Rolled Steel

Follow standard good painting procedures. Be sure all surfaces are dry and clean. Remove loose dust, paint, grease, and oil residue from untreated surface. If sand-blasted, use Crystal Amber No. 3, sand, fresh water washed stock No. 5350-543-4398, and 80-100 psi air pressure. No scale should be present on the surface. Final treatment utilizes a methyl ethyl ketone wash followed by rinsing with Freon TF degreaser (Miller-Stephenson 180 or equivalent). Surfaces are allowed to air-dry and, if necessary, they may be treated with corrosion resistant zinc chromate primer meeting Federal Specification TT-P-664b or Red Lead Primer 13-k-51 from Mobile Chemical Company, conforming to Federal Specification TT-P-86e, Type 3.

9.1.2 Aluminum

Follow standard good painting procedures. Treat surface of aluminum by scrubbing with scouring powder and water. Flush liberally with water and observe for water break-free surface. If surface is not water break-free, repeat scrubbing and flushing procedure. When water break-free surface is obtained, flush surface with trichloroethane and allow surface to air dry. Handle cleaned surface with care. Avoid contact with dust, oils, and grease. If corrosion resistant primer is desired, use zinc chromate primer conforming to Federal Specification TT-P-666B. If anodizing of aluminum is required, the treatment shall conform to MIL-A-8625. For an Alodine treated surface, the aluminum shall conform to MIL-C-5541.

9.1.3 Glass

Follow standard good painting procedures. Glass is cleaned by first wiping the surface with methyl ethyl ketone, followed by a rinse with Freon TF degreaser (Miller-Stephenson 180 or equivalent).

9.2 Molding

The M-30 Thermal Protective coating is produced in the form of molded sheets, either flat or curved, as required.

To mold a sheet requires a molding die and a press capable of exerting a minimum of 100 psi on the part at 200°F. The required amount of catalyzed M-30 (Parts A and B mixed) is added to the release coated mold. The material is preheated in an open mold for 10 minutes at approximately 170°F mold temperature. Then the mold is closed quickly, and pressure is released, several times. This is done to aid in expelling entrapped air. After approximately three openings and closings of the mold the mold is pressurized to approximately 100 psi before closing the landed mold. It is held under pressure long enough for the material to reach approximately 160°F and then held for 20 minutes. This time period must be determined experimentally, since it is dependent on the mold and press characteristics.

After the material has been held for the required period of time it is cooled to approximately room temperature after which it is opened, and the molded sheet is extracted. If a flat sheet has been molded, and a curved sheet is required, it may be curved at this point. The sheet to be curved is simply placed on a mandrel, and under vacuum bag pressure is cured at least 24 hours at room temperature. If it is desired, the sheet may be bonded at this point, by using catalyzed, uncured M-30 as the adhesive or other approximately evaluated adhesive. NOTE: When bonding, the sheet surface to be adhered must be lightly sanded, and washed with acetone, MEK or toluene to remove all traces of the parting agent.

10.0 QUALITY ASSURANCE PROVISIONS

10.1 Responsibility for Inspection

Unless otherwise specified in the contract or the purchase order, the supplier is responsible for the performance of all the inspection requirements as specified herein. The supplier may utilize his own facility or any commercial laboratory acceptable to ARC. The processing activity, or its designated representative, reserves the right to perform any or all of the inspections set forth in the specification where such inspections are deemed necessary to ensure that supplies and services conform to prescribed requirements.

10.2 Classification of Examinations and Tests

All of the examinations and testing of the thermal protection coating shall be classified as qualification tests. Qualification tests shall be performed on samples submitted for approval as qualified products and shall be performed on individual lots of products submitted for acceptance. The qualification tests are listed in Table 2. A certified test report from the supplier shall accompany each product submitted for approval and each lot of thermal protection coating submitted for acceptance.

10.3 Sampling

Samples for product qualification or for qualified lot acceptance shall be as specified in Paragraph 10.3.2. The material preparation shall conform to the requirements of Paragraph 4.2 herein. A test report from the supplier shall accompany each sample to be tested, and shall show the composition number and the test results for all requirements of this specification and shall refer specifically to the applicable paragraphs herein. All the thermal protection coating manufactured and formulated as one batch shall be considered a lot and shall be numbered as such for purposes of inspection.

TABLE 2. QUALIFICATION TESTS

Examination or Test	Requirement	Test Method
Material	4.2	10.3.3.1
Appearance	4.3.1.1	10.3.3.1
Tensile Strength	4.3.1.2	10.3.3.2
Density	4.3.1.3	10.3.3.3
Temperature of Intumescense and Char Yield	4.3.1.4	10.3.3.4
Abrasion Resistance	4.3.1.5	10.3.3.5
Flexibility	4.3.1.6	10.3.3.6
Linear Expansion	4.3.1.7	10.3.3.7
Thermal Efficiency	4.3.1.8	10.3.3.8

10.3.1 Rejection and Retest

Failure of any lot to conform to all applicable requirements of this specification shall be cause for retest. Property or properties in question shall be retested on new specimens prepared from the same lot of thermal protection coating. If the results of tests of the second sample fail to meet the specification requirements, the entire lot shall be rejected.

10.3.2 Specimens

All samples to be tested shall be coated with the thermal protection coating at a minimum dry film thickness of 0.060 inch on cold rolled steel panels or as free films.

10.3.2.1 Size and Number of Specimens. The size and number of specimens for conformance to each requirement is indicated in Table 3, Page .

10.3.3 Test Methods

Unless otherwise specified, all examinations and tests shall be performed with a thermal protection coating conditioned for a minimum of 7 days, or 170 hours, at a temperature of 73.5 ±3.5°F and a R.H. of 50 ±5 percent.

10.3.3.1 Visual Inspection. Visual inspection shall be performed to determine the appearance requirements of Paragraph 4.3.1.1.

10.3.3.2 Tensile Strength. The tensile strength of the thermal protection coating shall be determined in accordance with ASTM D D638, except that the coating shall be molded to a thickness of 0.060 ±0.005 inch.

10.3.3.3 Density. The density of the thermal protection coating shall be determined in accordance with ASTM D 792, Method A1 and the results shall conform to Paragraph 4.3.1.3.

10.3.3.4 Temperature of Intumescence and Char Yield. The temperature of intumescence and char yield of the thermal protection coating shall be determined according to the following procedure and the results shall conform to Paragraph 4.3.1.4.

TABLE 3. TEST SPECIMENS

Test	Substrate Size, Inches	Number of Specimens	Requirement	Test Method
Appearance	3 x 3 x 1/16	1	4.3.1.1	10.3.3.1
Tensile Strength	6 x 6 x 0.060 molded sheet	2	4.3.1.2	10.3.3.2
Density	Use above	-	4.3.1.3	10.3.3.3
Temperature of Intumescence and Char Yield	Use above	-	4.3.1.4	10.3.3.4
Abrasion Resistance	4-1/8 x 1/16 disc CRS with 1/4 hole in center	6	4.3.1.5	10.3.3.5
Flexibility	3 x 3 x 0.032 Al O-condition	-	4.3.1.6	10.3.3.6
Linear Expansion	3 x 3 x 1/16 CRS	4	4.3.1.7	10.3.3.7
Thermal Efficiency	3 x 3 x 1/16 CRS with center disc (see 10.3.3.8)	2	4.3.1.8	10.3.3.8

Procedure: Using a thermogravimetric analysis (TGA) apparatus, record the weight loss versus temperature for the coating at a heating rate of 5°F/minute in a nitrogen atmosphere to 2100°F. Report the char yield (Y_c) as the percent weight fraction remaining at 1112°F, and the temperature of intumescence as the range where the weight loss is greatest.

10.3.3.5 Abrasion Resistance. The abrasion resistance of the thermal protection coating shall be determined using a Taber Abraser with a CS-17 Calibrase wheel and 1000 gm load and the results shall conform to Paragraph 4.3.1.5.

10.3.3.6 Flexibility. The flexibility of the thermal protection coating shall be determined according to the following procedure and the results shall conform to Paragraph 4.3.1.6.

Procedure: Using a Gardner Light Duty Impact Tester, IG-115, a 1/4 in. radius end, two pound impact rod is allowed to fall a calibrated distance (measured in feet) upon the coated side of the specimen panel. The inch-lb of energy is increased until coating adhesion failure occurs. The greatest energy tolerable is reported in inch-lb.

10.3.3.7 Linear Expansion (Intumescence). The linear expansion of the thermal protection coating shall be determined according to the following procedure and the results shall conform to Paragraph 4.3.1.7.

Procedure: The edges of the test specimen as well as a 1/8 inch perimeter overlap of the coating and the exposed cold rolled steel substrate shall be brushed with a red lead primer meeting Federal Specification TT-P-86e, Type 3, to minimize corrosion of the unocated edges. Two of the four specimens are further conditioned for seven days at 100 ±3.5°F and 90 ±2 percent R.H. The coating specimens are placed coating side up in an oven preheated to 660°F and allowed to remain for 30 minutes. Gases should be vented from the oven. Remove after 30 minute period, allow to cool, then calculate the linear expansion:

$$\text{Linear Expansion} = \frac{Tf - Ti}{Ti}$$

where

Tf = Average thickness of coating after intumescence, inches

Ti = Initial coating thickness, inches

10.3.3.8 Thermal Efficiency. Thermal efficiency of the thermal protection coating shall be determined according to the following procedure and the results shall conform to Paragraph 4.3.1.8.

Procedure: This test, to be performed at ARC, exposes the coating to a fire environment where a total flux of 10 Btu/ft^2-sec is 90 percent radiative in a slightly fuel rich condition. Aviation fuel (JP-4) is used to fire the unit. The specimens are prepared on special 3" x 3" x 1/16" cold rolled steel substrates. That is, a 1 inch diameter hole in the center of the panel has a 15/16 inch diameter 1/16 inch thick cold rolled steel disc cemented in place with epoxy novolac. This provides a higher thermal resistance to reduce thermal conductance effects from the edges of the specimen panel. The coated panel thickness is measured and recorded and the panel preconditioned to Paragraph 10.3.3 or other special environments and when ready to test is inserted in a transite mask or holder which allows the panel to rest on about 1/16 inch to 1/8 inch of the edges of the coated surface. At time, t = 0, the masked panel is placed over the fire box and a thermocouple in contact with the back of the panel records the temperature rise of the center disc in the panel. The flux is uniform over the entire panel and the center disc is about 8-10 percent of the exposed area and is representative of a lrager, semi-infinite panel. From the time-temperature history thus obtained, and the thickness in mils of coating tested, one reports the time in seconds to reach a given temperature and the mil thickness coating. Since the flame environment is a more severe test of the coatings, the intumescent thickness is also reported after this test.