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FORMULATION AND PRODUCTION OF
INTUMESCENT COATING SYSTEMS

By Jack Hoffman and Harry R. Schwartz

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FORMULATION AND PRODUCTION OF
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Hughes Aircraft Co.

I SUMMARY

The purpose of this program was to develop manufacturing methods and produce substantial quantities of fire protective intumescent coatings based on NASA-Ames formulas 45B3 and 313. Individual batches as large as 114 liters (30 gal) were manufactured at the facilities of Furane Plastics, Inc.

The coatings consist of three reactive parts mixed together at the time of use. Part A is a mixture of polysulfide resin, intumescent salt and MEK; Part B is composed of epoxy resin and toluene; and Part C contains the curing agent tri(dimethylamino methyl)phenol in toluene. Formulas 45B3 and 313 are the same except for addition of Refrasil fibers to the 313 material.

A source of high quality intumescent salt (i. e., the ammonium salt of 4-nitroaniline-2-sulfonic acid) which met the requirements of NASA Specification A-16839(E) Rev. 1. was found at Allied Chemical Corporation. Three hundred sixty two kg (800 lb) of salt was procured at \$11.00/kg (\$5.00/lb) which was 1/4 the cost of previously available material.

Three production methods were investigated for making Part A (i. e., polysulfide resin, salt, MEK mixture) of the intumescent coatings in lots of up to 114 liters (30 gal). These were: Koruma milling (i. e., a high speed stone mill), Stud-milling the salt (i. e., an impact type dry particle reducer followed by Ystral mixing (i. e., a propeller-in-funnel type disperser), and ball-milling. Of the three methods, ball milling gave the best control of particle size reduction, thixotropy and elimination of air or moisture entrainment. By holding back a portion of the solvent (for rinsing the mill) and grinding for only 2-1/2 hours, yields of 93 percent were obtained. Thus, ball-milling is considered to be a suitable and an economical method of manufacture.

Thermal performance of coatings produced by Ystral mixing Part A was not as good as that produced by ball milling. Coatings produced from ball-milled Part A all met the 78.8 sec/mm (2.0 sec/mil) thermal efficiency requirement.

Part A material was found to react with tin coated steel containers to form a black deposit of presumably tin and/or iron sulfide. A baked resin coating on the interior of the tinned steel containers was only partially effective in inhibiting the black deposit formation, and Part A was subsequently packaged in glass jars.

Gelation of Part A packaged in cans with a large air ullage was observed in less than 6 weeks after manufacture. Partial polymerization of Part A during

storage was suspected as the cause of the poor thermal performance of the first batch. To avoid this problem, subsequent production batches were packaged in containers approximately 90 percent full with the ullage swept out by dry nitrogen.

Several batches of a new NASA formulation, "Flexible Thermal Protection Coating", were produced, and a number of sheets of this material prepared by spraying multiple coats. The sheets were 9.45 X 9.45 cm (24 X 24 in.) with a minimum thickness of 81 mm (32 mils). In two of the sheets a 0.18 mm (7 mil) layer of MIL-Y-1140 glass veil mat was imbedded in the sheet during manufacture.

A number of plywood panels were coated with 45B3 Thermal Protection Coating and one 4.4 cm (1-1/2 in.) diameter by 38.1 cm (15 in.) long fuel hose was coated with Flexible Thermal Protection Coating.

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II INTRODUCTION

Intumescent coatings, i. e., coatings which expand when heated, have been used as protective coverings for flammable materials and to reduce fire damage to non-flammable materials. On heating, the coating expands to many times its original thickness. Improved thermal insulation is provided by the formation of a closed cell porous structure filled with low thermal conductivity gases.

Major advances in the field were made by Parker, Riccitiello, Sawko and Fohlen in work conducted at NASA Ames Research Center, Moffett Field, California. In their research, an improved intumescent agent, the ammonium salt of 4-nitroaniline-2-sulfonic acid, was developed. Intumescent coatings formulated with this salt by Riccitiello and Sawko have been extremely effective in preventing the spread of fires, even in relatively thin films of 1.52 mm (60 mils). These coatings have a wide variety of potential military and commercial applications typical of which are paints to protect ordnance (e. g., bombs and missiles), firewalls on ships, industrial facilities, and aircraft structures.

The primary purpose of this contract was to produce substantial quantities of two basic NASA coatings, designated 45B3 and 313. Material produced was intended for testing and as samples for potential users. It was expected that the experience gained in making these moderate quantities under actual manufacturing conditions (rather than on a laboratory scale) would provide the basis for future large scale, low cost production. Specific objectives of the contract were as follows:

(1) To procure or produce the intumescent salt (at as low a cost as possible) and perform the required qualification tests.

(2) To procure all other necessary ingredients required to produce the intumescent coatings and to perform the qualification tests on these materials.

(3) To compound and produce acceptable intumescent coating systems as set forth in the specifications in the quantities listed in the Statement of Work, or as designated by the Technical Monitor.

(4) To compound and produce acceptable intumescent coating systems which are based on the formulations provided in the specifications, but which are modified for specific applications as directed by the Technical Monitor.

(5) To characterize the physical, chemical and thermal properties of these ~~coating systems through quality control procedures during formulation of the coating, and through physical and thermal testing of coated specimens.~~

(6) To study other parameters of application of these coatings, such as substrate preparation, primers, top coats, methods and equipment for application.

(7) To apply these coatings on specific items when directed by the Technical Monitor.

(8) To document the formulation, production, quality control and testing procedures of the coating and the intumescent salt with the objective of obtaining consistent results.

To provide the program with paint production facilities, a contract was entered with Furane Plastics Inc., of Los Angeles, a local manufacturer of polymers and coatings with national distribution.

III. PRODUCTION OF INTUMESCENT COATINGS

Procurement and Qualification of Raw Materials

Intumescent salt. — Arrangements were made to purchase the ammonium salt of 4-nitroaniline-2-sulfonic acid from the Allied Chemical Corporation's Buffalo Dye Plant in 182 kg (400 lb.) lots. Although the salt was required to meet the more stringent Revision 1 of NASA specification A-16839 (E), Ref (1), the cost of \$11.00 per kg (\$5.00 per pound) was about 1/4 that of salt previously available.

The first shipment of salt received from Allied, Lot #0457751, Code 14237, contained large lumps several inches across. Analysis of the salt disclosed ammonium sulfate and water content in excess of specification limits (see Table I). After considerable testing, it was determined that there was a marked difference in ammonium sulfate content among the four 45.4 kg (100 lb) drums and from powdered salt to lumpy salt (see Table II).

This lot was rejected and a new 181.6 kg (400 lb) shipment, Batch No.0657731 was received July 7, 1971. Analysis of this batch showed that it met all of the requirements of NASA Specification A-16839 (E) Rev. 1 except for a slight excess of water and particle size (see Table III). Since the water content was acceptable to the NASA Technical Monitor, and Ames Research Center had given Allied Chemical permission to deviate from the particle size requirement, the salt was qualified.

The second order of 181.6 kg (400 lbs) of salt received in early October, 1971 was found to be contaminated with what appeared to be slivers of charred wood or plastic. Some of these particles were as long as 0.95 cm (3/8 inch) and as thick as 1.27 mm (0.050 inches). This batch of salt was also rejected and subsequently replaced by 90.8 kg, of Batch No. 0657731 received 10-30-71, and 90.8 kg of Batch No. 0657731 received 1-20-72. Unfortunately all batches received by HAC (Hughes Aircraft Co), except for the very first, were given the same batch number by the manufacturer. As a consequence, it was necessary to use the receipt date as a means of identification.

TABLE I

ANALYSIS OF 4-NITROANILINE-2-SULFONIC ACID AMMONIUM
SALT, BATCH NO. 0457751, CODE 14237

Property	Spec. A-16839(E) Rev. 1 Requirements	Test Results (Average)
IR Spectrum	Figure in spec.	—
Physical Appearance	Yellow, free-flowing, granular	Yellow, free-flowing, granular plus lumps
Particle Size	No particles above 200 μ .	Mixture of powder <200 μ and very large lumps (easily crushed)
Density	1.686 g/cc \pm 0.01	1.687 g/cc
Equivalent Weight	235 \pm 12	243
Initial Decomposition Temperature	285 \pm 18°C	300°C
Purity: (1) 1. Carbon, Hydrogen and Nitrogen	C, 30.7 \pm 1.3% H, 3.9 \pm 0.2% N, 17.9 \pm 0.8%	C, 30.84% H, 4.22% N, 17.27%
(2) 2. Ammonium Sulfate	Less than 0.5%	1.4%
(3) 3. Chloride	Less than 0.5%	0.18%
(4) 4. Water	Less than 0.06%	0.20%

¹C, H and N determined by combustion microanalysis

²Sulfate determined by gravimetric BaSO₄

³Chloride determined by gravimetric AgCl

⁴Water determined by Karl Fischer analysis

TABLE II

AMMONIUM SULFATE ANALYSIS OF VARIOUS
INTUMESCENT SALT SAMPLES
BATCH NO. 0457751, CODE 14237

<u>Sample Description</u>	<u>Performed by</u>	<u>Test Method⁽¹⁾</u>	<u>(NH₄)₂SO₄, %</u>
a. Preshipment	Allied	Allied	<0.1
b. Retain of preshipment	Allied	Allied	0.15
c. "X", drum unknown	HAC	HAC	1.4
d. "X", drum unknown	HAC	Allied	2.2
e. "X", drum unknown	Allied	Allied	2.3
f. Powder from Drum #1	HAC	HAC	0.62
g. Lumps from Drum #1	HAC	HAC	1.9
h. Powder from Drum #2	HAC	HAC	0.74
i. Lumps from Drum #2	HAC	HAC	3.2
j. Powder from Drum #3	HAC	HAC	0.37
k. Lumps from Drum #3	HAC	HAC	1.0
l. Powder from Drum #4	HAC	HAC	1.2
m. Lumps from Drum #4	HAC	HAC	5.3

¹HAC and Allied test methods utilize similar procedures of precipitating BaSO₄ for gravimetric analysis. The methods, however, have significant differences (e.g., Allied uses a greater excess of BaCl₂ and filters through a coarser paper than does HAC).

TABLE III

ANALYSIS OF 4-NITROANILINE-2-SULFONIC ACID AMMONIUM
SALT, BATCH NO. 0657731, RECEIVED 7-7-71

Property	Spec. A-16839(E) Rev. 1 Requirements	Test Results (Average)
IR Spectrum	Figure in spec.	Matches curve
Physical Appearance	Yellow, free-flowing, granular	Yellow, free-flowing, granular
Particle Size	No particles above 200 μ .	99.99% under 200 μ ⁽⁵⁾
Density	1.686 g/cc \pm 0.01	1.680 g/cc
Equivalent Weight	235 \pm 12	236
Initial Decomposition Temperature	285 \pm 18°C	285
Purity: 1. Carbon, Hydrogen ⁽¹⁾ and Nitrogen	C, 30.7 \pm 1.2% H, 3.9 \pm 0.2% N, 17.9 \pm 0.8%	C, 30.64% H, 4.11% N, 17.14%
2. Ammonium Sulfate ⁽²⁾	Less than 0.5%	Drum #1 0.018% Drum #2 0.018% ⁽⁶⁾ Drum #3 0.010% Drum #4 0.015%
3. Chloride ⁽³⁾	Less than 0.5%	0.051%
4. Water ⁽⁴⁾	Less than 0.06%	0.10%

¹C, H and N determined by combustion microanalysis

²Sulfate determined by gravimetric BaSO₄

³Chloride determined by gravimetric AgCl

⁴Water determined by Karl Fischer analysis

⁵Ames Research Laboratory gave Allied Chemical Co., permission to produce salt with a particle size of 20 mesh or finer (i.e., \leq 840 μ or 0.033 inches)

⁶(NH₄)₂SO₄ content of same dissolved salt sample was 0.010% using Allied Chemical Corporation's test method. This is within experimental limits of the HAC method value of 0.018%.

Batch No. 0657731 received 10-30-71 met all the requirements except for particle size and was accepted (see Table IV). Batch No. 0657731 received 1-20-71 had marginal values for density, nitrogen and contained a very small amount of insoluble material; however, these were not significant variations, and the Technical Monitor agreed that the salt should be accepted (see Table V for test results).

All salt qualification tests were performed in accordance with NASA Specification A-16839(E) Rev 1. Where a specific procedure was not described, a standard chemical analysis method was employed. These were as follows:

- (1) C, H and N by combustion microanalysis
- (2) Chloride by gravimetric Ag Cl (See Appendix A for detail procedure)
- (3) Sulfate by gravimetric Ba SO₄ (See Appendix A for detail procedure)
- (4) Water by Karl Fischer analysis
- (5) Density by displacement in CCl₄

A comparison of the two ammonium sulfate analysis methods (i.e., HAC's and Allied Chemical Corporation's) was inconclusive (see Table III). Using HAC's method the ammonium sulfate content was 0.018 percent compared to 0.010 percent using Allied Chemical's method. The test was performed on the same dissolved salt solution to preclude variations in the dry salt. Because the high purity of the salt yielded such a small amount of precipitate, differences in the test methods (e.g., in filtration) were masked. Since the ammonium sulfate content is so low (and also should be low for future batches of intumescent salt) the analysis method (i.e., HAC versus Allied) as related to specification limits is not significant.

TABLE IV

ANALYSIS OF 4-NITROANILINE-2-SULFONIC ACID AMMONIUM SALT
BATCH NO. 0657731, RECEIVED 10-30-71

Property	Spec. A-16839(E) Rev. 1 Requirements	Test Results (Average)
IR Spectrum	Figure in spec.	Matches curve
Physical Appearance	Yellow, free-flowing, granular	Yellow, free-flowing granular
Particle Size	No particles above 200 μ .	0.5% of particles ⁽¹⁾ above 10 μ exceed 200 μ . Some agglomerated larger particles
Density	1.686 g/cc \pm 0.01	1.68 g/cc
Equivalent Weight	235 \pm 12	242
Initial Decomposition Temperature	285 \pm 18°C	275°C
Purity:		
1. Carbon, Hydrogen and Nitrogen	C, 30.7 \pm 1.2% H, 3.9 \pm 0.2% N, 17.9 \pm 0.8%	C, 30.61% H, 3.80% N, 17.86%
2. Ammonium Sulfate	Less than 0.5%	0.004%
3. Chloride	Less than 0.05%	0.045%
4. Water	Less than 0.06%	0.06%

(1) Ames Research Laboratory gave Allied Chemical Co. permission to produce salt with a particle size of 20 mesh or finer (i.e. \leq 840 μ or 0.033 inches).

TABLE V

ANALYSIS OF 4-NITROANILINE-2-SULFONIC ACID AMMONIUM
SALT, BATCH NO. 0657731, RECEIVED 1-20-72

Tests	Spec A-16839(E) Rev. 1 Requirements	Test Results (Average)
IR Spectrum	Figure in Spec	Matches curve
Physical Appearance	Yellow free-flowing granular solid	Yellow free-flowing granular solid
Particle Size	No particles above 200 μ	0.8% of particles ⁽¹⁾ above 10 μ exceed 200 μ .
Density	1.686 g/cc \pm 0.01	1.672 g/cc
Equivalent Weight	235 \pm 12	240
Initial decomposition temperature	285 \pm 18°C	275°C
Carbon, Hydrogen, and Nitrogen	C, 30.7 \pm 1.2% H, 3.9 \pm 0.2% N, 17.9 \pm 0.8%	C, 30.7% H, 4.1% N, 18.9%
Ammonium Sulfate	Less than 0.5%	0.06%
Chloride	Less than 0.5%	0.08%
Water	Less than 0.06%	0.06%

¹ 0.01 percent of salt is insoluble, heavier than water, non-magnetic, mostly dark or black, with fibrous and stone-like particles

Resins, curing agent and solvents. — Resins, curing agent and solvents for the entire contract were procured from the sources recommended in NASA Specifications A-16839(A) and (C), Ref. 2 and 3. These materials were as follows:

TABLE VI
SOURCE OF RESINS, CURING AGENT AND SOLVENTS

Material	Lot No.	Source
Polysulfide polymer, liquid, LP-3 (Product specification code LF-241)	289M 302M ⁽¹⁾	Thiokol Chemical Corp.
Epoxy resin, liquid, Epon 828 (Bulletin SC: 60-146R)	2PHJ27	Shell Chemical Co.
2, 4, 6 tri (dimethylamino methyl) phenol, DMP-30	2-9774	Rohm and Haas
Methyl ethyl ketone, TT-M-00261C	-	McKessen Chemical Co.
Toluene, TT-T-548C	-	L.T. Sawyer Co.

¹ 18.9 liter (5 gal) of LP-3 Lot No. 302M was ordered for last production batch of 45B3/313 (combined) Lot No. 2-23-72.

Except for the polysulfide resin, only one lot of each material was purchased and used throughout the entire program. All materials used were tested at Furane Plastics Inc., and met the requirements of Specifications A-16839(A) and (C). See Appendix B for original test results obtained June 2, 1971. The materials were retested August 25, 1971 and again for the last time on 10-18-71. None of the raw materials showed any significant change in properties during the above interval.

To complete the last production batch of intumescent coating, an additional five gallons of LP-3 polysulfide resin was obtained and qualified (see Appendix B).

Refrasil fibers. — 23.1 kg (51 pounds) of Refrasil (chemically leached glass) fibers were purchased from the H.I. Thompson Co. (HITCO) and tested in accordance with paragraph 3.7 of NASA Specification A-16839(C). Reference (3). The Refrasil fibers #F100-1/16-1/32-1/64 (P.O. #X-4-346924-F94) were sampled from the top, center and bottom of the drum. A small portion of each sample was combined and mixed with a large volume of Freon TF solvent. After the Refrasil-Freon mixture was passed through a Millipore filter, a microscopic particle analysis was made. Results of this analysis were as follows:

TABLE VII
PARTICLE SIZE ANALYSIS OF REFRASIL FIBERS

Fiber Characteristic	Specification Requirement	Test Result
Diameter	0.0004-0.0005 inch	0.00030-0.00051 inch
Length distribution	~10% 0.003 inch ~10% 0.030 inch ~80% nominal 0.01 inch	7.5% < 0.003 inch 7.5% > 0.030 inch 85.0% 0.003-0.030 inch

As can be seen from the analysis, the length distribution meets the specification. Although the fiber diameter range is slightly greater than the specification limits, it was acceptable to the Technical Monitor. The smaller diameter fibers should pose no problem in manufacturing the intumescent paint nor are they expected to affect the performance of the applied coating. Since Hammer milling of the Refrasil (as required by Specification A-16839 (D), Reference (4) for manufacture of the 313 Thermal Protection Coating) would increase the number of short fibers, permission was obtained from the Technical Monitor to use the Refrasil "as-is".

A slight "off-white" color of the Refrasil on the top of the drum was observed. The Refrasil obtained from the center and bottom of the container did not exhibit this discoloration. HITCO said that this is a normal occurrence and that they have never experienced or heard of any problems related to use of the "off-color" material.

Manufacture of 45B3 and 313 Coatings

General approach.— As previously stated, the primary purpose of this program was to produce substantial quantities of 45B3 and 313 Thermal Protection Coatings. The formulas for these coatings as specified in Specifications A-16839 (B) and (D), References (5) and (4) are presented below:

<u>Material</u>	<u>Parts by Weight</u>	
	<u>45B3</u>	<u>313</u>
<u>Part A</u>		
Polysulfide Polymer, Liquid (LP-3)	14.1	10.7
Ammonium salt of 4-nitroaniline-2-sulfonic acid	57.0	43.3
Methyl Ethyl Ketone	28.9	22.0
Refrasil Fibers	-	5.5

<u>Material</u>	<u>Parts by Weight</u>	
	<u>45B3</u>	<u>313</u>
<u>Part B</u>		
Epoxy Resin, Liquid (Epon 828)	14.1	10.7
Toluene	4.7	3.6
<u>Part C</u>		
Tri (dimethylamino methyl) phenol (DMP-30)	2.8	2.1
Toluene	2.8	2.1

During the program, three principal methods of manufacturing the 45B3 and 313 thermal protection coating were investigated. Table VIII lists the several production lots, along with the method of manufacture and quantity obtained.

The original plan for manufacture of the 45B3 coating was to premix the ingredients of Part A (i.e., polysulfide resin, intumescent salt and MEK) and to mill this mixture in a Koruma mill to a 1 + fineness of grind on the Hegman Gauge. The Koruma mill utilizes two flat horizontal stones set at a predetermined gap with the lower stone rotating at 3000 rpm (see Appendix C). In operation the Koruma mill is very similar to the Morehouse mill recommended in Specification No. A-16839(D), Reference 4.

As explained in the following paragraphs, this method was abandoned when it was found that the large particles of salt plugged the mill.

The second method of manufacture was utilized to prepare several batches of 45B3, 313 and flexible coating. The method required that the dry salt be first reduced in particle size by Stud-milling and then dispersed in the vehicle for Part A with a high speed Ystral Jet mixer (see Appendix C).

The third and final method used was ball-milling. Because several problems were encountered with the 45B3 coating produced by Ystral mixing of the Stud-milled salt (e.g., low thermal efficiency), an efficient method of Ball milling was developed (i.e., one which gave a high yield). Satisfactory 45B3 and 313 coatings were produced by this procedure.

Problems encountered in Koruma milling of 45B3 coating. — To properly charge the Koruma mill, a pre-mix of Part A (i.e., the polysulfide resin, intumescent salt and MEK) was prepared. One of the problems encountered involved the order and method used in premixing Part A. It was discovered that the LP-3 polysulfide had to be diluted with the MEK before addition of the intumescent salt. Addition of the salt directly to the undiluted polysulfide resin during premixing produced a nonuniform mixture with large agglomerates of unwetted salt. Later addition of the required amount of solvent did not significantly alter this condition.

TABLE VIII

PRODUCTION BATCHES OF 45B3 AND 313 THERMAL
PROTECTION COATINGS

Coating	Lot No.	Quantity Manufactured	Method of Manufacture	Salt Batch ⁽¹⁾
45B3	7-26-71 ⁽²⁾	45.5 liter (12 gal)	Koruma milling	7-7-71
45B3	8-18-71 ⁽³⁾	45.5 liter (12 gal)	Ystral mixer ⁽⁴⁾	7-7-71
313	9-2-71 ⁽³⁾	45.5 liter (12 gal)	Ystral mixer ⁽⁴⁾	7-7-71
45B3	11-5-71	18.9 liter (5 gal)	Ystral mixer	7-7-71
45B3	12-8-71	28.4 liter (7.5 gal)	Ball milling	10-30-71
313	12-8-71	43.5 liter (11.5 gal)	Ball milling	10-30-71
45B3	2-7-72	77.5 liter (20.5 gal)	Ball milling	10-30-71
45B3	2-23-72	56.8 liter (15 gal)	Ball milling	1-20-72
313	2-23-72	56.8 liter (15 gal)	Ball milling	1-20-72

¹Intumescent salt batches were identified by the date received since they all had the same Allied Chemical Corp. batch number (i. e., No. 0657731). Salt batch 7-7-71 was Stud-milled twice (at Furane Plastics Inc) to reduce particle size.

²Lot 7-26-71 scrapped because of partial intumescence during grinding

³Failed to meet thermal efficiency requirements

⁴Prechilled MEK and mixing vessel used for manufacture of Part A.

Because of the relatively coarse particle size of the as-received salt, pre-mixing with the Ystral Jet mixer did not produce a uniform dispersion of Part A. Thirty minutes of processing in a Morehouse-Cowles high speed kinetic dispersion unit also resulted in a mixture in which the larger salt particles dropped out rapidly.

Subsequent attempts to grind this Part A (i. e., the nonhomogeneous polysulfide-salt-MEK mixture) in the Koruma mill were unsuccessful and resulted in loss of the batch. Although the Koruma mill was water cooled and the grinding stones were set for a loose pass (i. e., 127 μ or 5 mils apart), overheating took place as evidenced by intumescence of a portion of the batch in the mill. The initial portion of the premix containing the dispersed finer particles of salt passed through the mill without too much difficulty. Plugging and overheating of the mill occurred when the last portion of the premix containing the coarse salt particles was introduced. At that juncture, attempts to manufacture the 45B3 coating at Furane were stopped, and a laboratory investigation into alternate paint preparation methods was started at Hughes.

Laboratory investigation of alternate methods of manufacture. - During the laboratory investigation, it was found that the salt could be dispersed reasonably well if the polysulfide was first diluted with MEK. However, because of the particle size of the salt, it tended to settle out fairly rapidly even in this mixture. If the Koruma mill were to be used, it would have been necessary to keep the mixture under continuous agitation while feeding the mill.

Ball milling of 45B3 Part A (which is recommended in NASA Specification No. 16839B) was next attempted using a 0.95 l (1 quart) laboratory mill. After premixing Part A with "Lightnin" (i.e., propeller blade type) mixer, the mixture was ball milled. In four hours of milling, a grind of 1 - 2 was achieved. However, the mixture became thixotropic, and removal from the mill was extremely difficult because of the lack of flow. Longer milling increased the thixotropy while a shorter time was not sufficient to produce a 1 + grind. Rinsing the mill with solvent was imperative to avoid a considerable loss of material (i.e., 50 percent), but this resulted in a solids content for Part A below specification requirements. Several attempts were made to ball mill Part A with a portion of the solvent held back for rinsing out the mill but with only partial success. When sufficient solvent was held out for adequate rinsing, the mixture was too viscous to mill (i.e., the balls would not tumble). Conversely, when sufficient solvent was left in Part A for proper milling, the amount held out was inadequate for complete rinsing and a yield of only 70 - 80 percent was obtained.

Ball milling, of course, would be a satisfactory method of manufacture if additional solvent could be added to the formula described in Specification A-16839 (B). Since additional solvent was not permitted and removal of excess solvent would have been impractical for large quantities, ball milling was abandoned for the time being.

Ystral mixing of 45B3 coating (Lot 8-18-71) using Stud-milled salt. - In view of the problems encountered, a manufacturing technique different from those previously described was employed for the first 45.5 liter (12 gal) production batch (Lot 8-18-71) of 45B3 coating. The procedure used to prepare Part A of Specification No. A-16839(B) consisted of the following steps:

(1) The dry salt was "Stud-milled" twice to break up the agglomerates and produce a powder considerably finer than the "as received" salt. Dry milling was performed with a Model 160Z Kolloplex Stud Mill manufactured by the Alpine American Company. Operation of the mill consists of introducing the dry salt into the center of a rotating disk studded with pins in several concentric rings. The rotating disk meshes with a similar pin studded stationary disk and the salt particles are flung against the pins by centrifugal force. See Appendix C, Figure 3. A sieve analysis of the twice Stud-milled salt showed 10 percent (as little balls) > 170 mesh, 68 percent < 170 mesh but > 325 mesh, and 22 percent < 325 mesh.

(2) The polysulfide resin was diluted with chilled MEK (to reduce evaporation) in a 56.8 liter (15 gal) stainless steel container. The two were blended with a "Lightnin" propeller type mixer for several minutes.

(3) While under low speed agitation, the salt was added at a slow, uniform rate to the diluted polysulfide and completely dispersed with the "Lightnin" mixer. Salt addition was accomplished over a period of one hour. The material was allowed to "wet out" (i.e., stand) for approximately one hour, redispersed and checked for fineness of grind which was 1 to 2. After straining through one layer of commercial cheese cloth, 3.61 kg (7.97 lbs) of Part A was packaged in each 7.6 l (2 gallon) pail.

The yield (i.e., quantity of coating obtained compared to the quantity of resin, salt and solvent used) was 96 percent for Part A. This compared favorably with the 70 - 80 percent yield obtained by ball milling.

Subsequent lots of coating made from Stud-milled salt employed the Ystral Jet mixer in lieu of the "Lightnin" mixer. Because of the more efficient action of the Ystral, the mixing time for addition of the salt to Part A was reduced from one hour (with "Lightnin" mixer) to 5 - 10 minutes of low speed plus 1 - 2 minutes of high speed Ystral mixing. The fineness of grind was the same (i.e., 1+).

For the reasons described under "Packaging of 45B3 and 313 coating kits", Part A of 45B3 (Lot 8-18-7) was packaged in 7.6 liter (2 gal) resin coated, tin plated steel pails leaving about 60 percent ullage. Each pail contained 3.62 kg (7.97 lbs) of 45B3 Part A. Subsequent lots of 45B3 Part A were packaged in full glass jars.

Part B (epoxy resin and toluene) was blended and the appropriate quantity (0.680 kg or 1.50 lbs) packaged in 0.950 liter (1 quart) friction top tin cans.

Part C (DMP 30 and toluene) was blended and the appropriate quantity packaged in 0.425 liter (1/2 pint) tin cans (i.e., 0.202 kg or 0.45 lbs).

Ystral mixing of 313 coating (Lot 9-02-71) using Stud-milled salt. - The first 45.5 liter (12 gal) batch of 313 coating was manufactured at Furane Plastics on 9-2-71. The method employed was similar to that used for manufacture of Part A of the 45B3 coating described above. Essential steps were as follows for manufacture of Part A, Specification A-16839(D).

(1) The dry salt was "Stud milled" twice.

(2) The polysulfide resin was diluted with chilled MEK and blended with the Ystral Jet Mixer in a water jacket container.

(3) While under low speed agitation the salt was slowly added over a period of 5 - 10 minutes after which the Ystral was operated at high speed for 1 - 2 minutes (a grind of 1+ was obtained).

(4) The mixer was operated at low speed while the Refrasil fibers were added slowly over a 5 - 10 minute span after which the mixer was operated again at high speed for 1 - 2 minutes.

(5) The material was allowed to wet out for approximately 30 minutes, redispersed, strained through one layer of commercial cheese cloth and packaged.

Packaging of the coating was similar to that described for 45B3 Lot 8-18-71 - Part A in 7.6 liter (2 gal) with approximately 60 percent ullage and Parts B and C in tin cans.

Ball milling 45B3 and 313 coatings. - Although Ystral milling produced a Part A which met the specification's material requirements (e.g., composition, grind, etc), the applied coating did not possess the desired thermal performance. A number of problem areas were uncovered (e.g., package stability) which may have been related to the Ystral mixing. At this point a complete change in manufacturing procedure was felt to be necessary. (These problems are discussed in the Section covering Qualification Testing.)

After performing a number of tests, it was concluded that ball milling of Part A would provide the best means of controlling the exposure to moisture and air during manufacture. It would provide a product with better particle uniformity and dispersion and less tendency for the salt to "settle-out".

By restricting the ball milling time to 2-1/2 hours the thixotropy could be controlled. This allowed the mill to be adequately rinsed by holding back some solvent and adding a small additional amount above the formula requirement. In this manner a good yield of 93 percent (i.e., based on material charge) was obtained in contrast to the 50 percent reported by Ames and the previous 80 percent obtained at HAC. The non-volatile content of Part A was within one percent of theoretical, and, more important, the thermal efficiency of the coating produced by ball milling in this fashion met specification requirements.

Procedure for ball milling of 45B3 and 313 coatings Lot 12-8-71. - Since the ratio of salt to polysulfide resin for Part A of both formulas (i.e., the 45B3 and 313 coatings) was the same, a "master batch" of approximately 60.6 liter (16 gal) of Part A was prepared. Because of the hard settling previously encountered with Part A of the 313 coating, it was decided to package the Refrasil fibers separately (Part A of the 45B3 coating does not require Refrasil). "As-received salt was employed rather than Stud-milled salt for manufacturing Part A in accordance with Specifications A-16839(B) and (D) as follows:

(1) A new 25 liter (6.6 gal) ceramic ball mill was purchased by the Furane Company specifically for this program. After cleaning the mill and ceramic balls (which filled 50 percent) by a "break-in" run with solvent and clean sand, the mill was thoroughly rinsed and the first of six batches was charged into the mill.

(2) The total required LP-3 for the six batches was blended with 75 percent of the required MEK by hand mixing. The remaining 25 percent of the MEK was held back for rinsing the mill after each load was removed.

(3) A mill charge representing approximately 35 percent of the 6.6 gallon volume consisted of the following:

1.73 kg (3.82 lbs) LP-3 resin	} blended
2.72 kg (6.00 lbs) MEK	
7.00 kg (15.44 lbs) salt	

0.91 kg (2.0 lbs) of MEK was used to rinse the mill after discharge.

(4) The LP-3/MEK blend was charged into the mill first and then the pre-weighed amount of salt added. The 34.3 cm (13.5 inch) I.D. mill was placed on the rollers and run at 44 - 45 RPM, slightly less than the desired 70 percent of critical speed. Calculation of critical speed was based on the formula provided in Specification No. A-16839B as follows:

$$\text{Critical Speed} = \frac{76.6}{\text{I.D. in feet}} = 68 \text{ RPM}$$

where Critical Speed is defined as the RPM at which unencumbered grinding media begin to centrifuge.

(5) After 2-1/2 hours of milling the grind was checked and the contents emptied into a clean 19 liter (5 gal) high density polyethylene container.

(6) The 0.91 kg (2 lbs) of MEK was added, the mill run for an additional 5 minutes and the rinsings added to original contents. After the rinsings were added, the ullage in the pail was purged with dry nitrogen and the containers sealed.

(7) The above procedure was repeated for each of the next five loads. An additional rinsing with 1.82 kg (4 lbs) of MEK was provided for the final load.

(8) All of the contents in the 19 liter (5 gal) pails were "master batched" with the Ystral mixer. A dry nitrogen head was maintained above the fluid during the operation. After 10 minutes of low speed mixing, filling of the individual glass jars was started. The Ystral mixer was in operation for all but the last five minutes of the filling operation which took a total of 40 minutes. Mixing was continued by hand during the last stage when the fluid level was too low to operate the Ystral.

(9) Each jar was topped-off with Part A to exactly 1049 gm (2 lbs, 5.0 oz) which left a minimum ullage for expansion.

(10) Part B was blended by manually stirring 3.48 kg (7 lb, 11 oz) of toluene into 10.42 kg (22 lb 15 oz) of Epon 828. The appropriate quantity (i.e., 198 gm or 7.0 oz) of Part B was weighed into individual metal containers.

(11) Part C was blended by manually stirring 2.06 kg (4 lbs 8.5 oz) of toluene into the same quantity of tri (dimethylamino methyl) phenol (i.e., DMP-30). The appropriate quantity (i.e., 57 gm or 2.0 oz) of this Part C was weighed into individual metal containers.

(12) Refrasil fibers (i.e., 72 gm or 2.7 oz) required for each kit of 313 coating were weighed into plastic bags, sealed and the bags inserted into metal containers.

Packaging of 45B3 and 313 coating kits. - Two types of containers were utilized for packaging Part A. The first, which was abandoned later, was a resin coated, tinned steel pail and the second was a glass jar. The initial selection of the metal container was made because of the problems in shipping glass containers containing highly flammable solvent (e.g., MEK).

Because of the observed rapid reaction of the Part A with unlined tin coated steel containers (a black deposit formed in less than two weeks), it was felt that lined (i.e., resin coated) tinned steel containers were essential. Only a few can coatings (e.g., Heresite*) would resist the MEK in Part A, and the only Heresite lined containers that could be readily obtained were 7.6 liter (2 gal) capacity. Since small quantities of the coating were required for sample distribution, it was decided to only partially fill (approximately 40 percent) the pails with sufficient Part A to make 3.785 liter (i.e., 1 gal) of mixed coating. This would provide sufficient space for thorough mixing of settled pigment and incorporation of parts B and C directly into Part A.

As was discovered later (see discussion of "Package stability of coating"), the large ullage was extremely detrimental. Also, it was found that the resin coating on the interior of the tin pail was not completely effective in preventing the formation of the black deposits.

For the above reasons the packaging of Part A in the metal pails was discontinued for the 45B3 and 313 coatings after the first production lot. Subsequent packaging of Part A was in 0.950 liter (1 quart) glass jars. The small ullage (approximately 10 percent of the total volume) left for expansion and mixing room was swept out with dry nitrogen before capping.

To provide a safe container for shipment, the padded glass jar of Part A and the cans of Part B and C were sealed in a 3.78 liter (1 gal) friction top paint can. Each kit contained the quantities of Parts A, B and C shown in Table IX.

TABLE IX
PACKAGING OF 45B3 AND 313 COATING KITS

Part	Net Weight 45B3 Kit	Net Weight 313 Kit
A	1049 gm (2 lbs 5.0 oz)	1049 gm (2 lbs 5.0 oz)
B	198 gm (7.0 oz)	198 gm (7.0 oz)
C	57 gm (2.0 oz)	57 gm (2.0 oz)
D	-	72 gm (2.7 oz)

Net volume of 45B3 kit is 1.06 liter (0.28 gal)

Net volume of 313 kit is 1.10 liter (0.29 gal)

Material properties of 45B3 and 313 coatings. - The following material properties were obtained on the respective production lots of coating. Property data are presented for Parts A, B and C in Table X.

*Baked phenolic/epoxy coating

MATERIAL PROPERTIES OF PRODUCTION LOTS OF 45B3 AND 313 COATINGS

Property	Requirement (1)	45B3 Lot 8-18-71	313 Lot 9-2-71	45B3 Lot 11-5-71	45B3 and 313 Lot 12-8-71	45B3 Lot 2-7-72	45B3 and 313 Lot 2-23-72
Part A: (2)							
Viscosity	600 - 1200 cps	-	1250 (3)	-	1750	1800	1320
Weight per gallon	10.3 ± 0.1 lbs/gal 1.24 ± 0.01 g/cc	-	10.28 ⁽³⁾ (1.23 g/cc)	10.28 (1.23 g/cc)	10.21 (1.23 g/cc)	10.21 (1.23 g/cc)	10.23 (1.24 g/cc)
Percent non-volatile	71.1 (min.)	71.7	-	72.2	70.1	71.09	70.0
Fineness of grind	1+	1+	1+	1+	3+	2-3	2-3
Part B:							
Viscosity	80 - 100 cps	-	87	90	89	85	96
Weight per gallon	8.9 ± 0.1 lbs/gal 1.07 ± 0.01 g/cc	-	8.90 (1.07 g/cc)	8.95 (1.07 g/cc)	8.96 (1.07 g/cc)	8.98 (1.08 g/cc)	8.94 (1.07 g/cc)
Part C:							
Viscosity	10 - 15 cps	-	12	-	12	15	16
Weight per gallon	7.6 ± 0.1 lbs/gal 0.91 ± 0.01 g/cc	-	7.58 (0.91 g/cc)	-	7.61 (0.91 g/cc)	7.63 (0.92 g/cc)	7.57 (0.91 g/cc)

¹Values are stated in (or calculated from) Specifications A-16839 (B) and (D)

²Requirements and data for Part A of 313 coating are before addition of Refrasil

³After addition of Refrasil, viscosity was 3000 cps and wt/gal was 1.28 g/cc (10.67 lbs/gal)

Qualification Testing of 45B3 and 313 Coatings

General description. - Qualification testing of the coatings was conducted in accordance with the procedures described in Specifications No. A-16839(B) and (D), Reference 5 and 4. Where the specifications did not define the exact test method or procedure, standard methods were used and are described in this text.

Thermal efficiency tests. - One major problem area involved the thermal efficiency test as related to the test apparatus and coating thickness. The test apparatus described in the NASA specifications was a JP-4 fuel fired furnace which was not available at HAC. Since a quartz lamp heat source had been used by HAC for testing similar thermal protection coatings (Reference 6), permission was obtained, in the contract, to use the quartz heating lamps (see Figure 1 and 2). These were operated at the required 10 Btu/ft²-sec which was 100 percent radiative rather than 90 percent radiative as specified for the NASA fuel furnace.

During the initial testing (i. e., 45B3 coating, Lot 8-18-71) it was found that the coating thickness required by the specification was too low to meet the thermal protection requirement. The A-16839(b) stated that the time for the back side of the 1.6 mm (1/16 in.) steel test panel having 0.76 - 0.81 mm (0.030 - 0.032 in.) thermal protection coating to reach 204°C (400°F) should be 95 sec or longer. The 45B3 Lot 8-18-71 coatings which were this thickness reached the 204°C temperature in 40 seconds.

Ultimately, the minimum thickness for the coating to be tested for thermal efficiency was set at 1.52 mm (0.060 in. or 60 mils), and the thermal efficiency was defined in terms of thickness as follows:

$$\text{Thermal efficiency} = \frac{\text{Seconds for metal back side to reach } 204^{\circ}\text{C}}{\text{Coating thickness in millimeters}}$$

or

$$\text{Thermal efficiency} = \frac{\text{Seconds for metal back side to reach } 400^{\circ}\text{F}}{\text{Coating thickness in mils}}$$

where

$$1 \text{ mm} = 39.4 \text{ mils}$$

For an acceptable coating, a thermal efficiency of 78.8 sec per mm of coating (2.0 sec per mil) or greater was required as measured on NASA's fuel furnace.

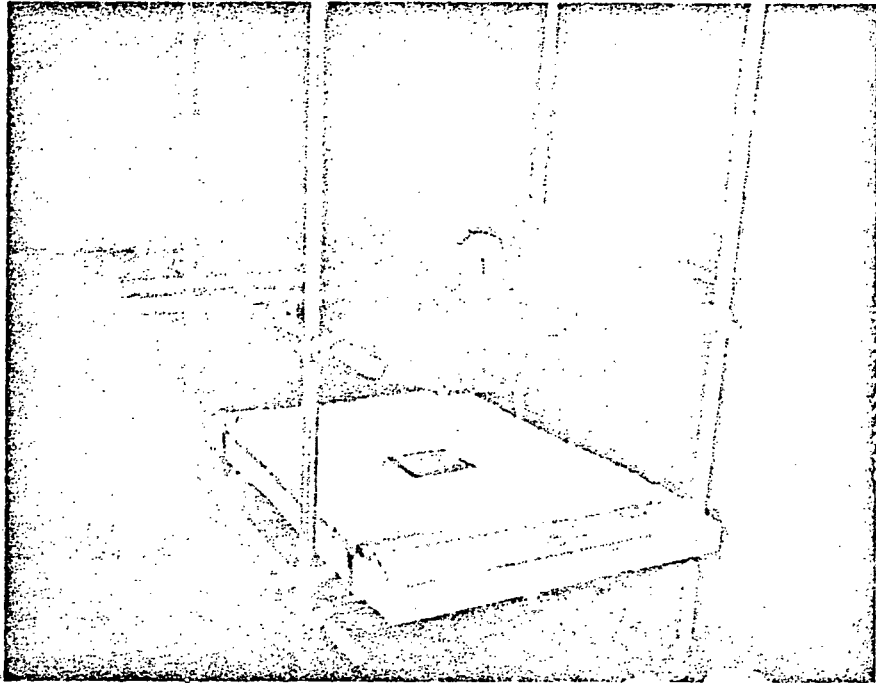


Figure 1. Quartz Lamp Heating Apparatus (Unexposed Specimen)

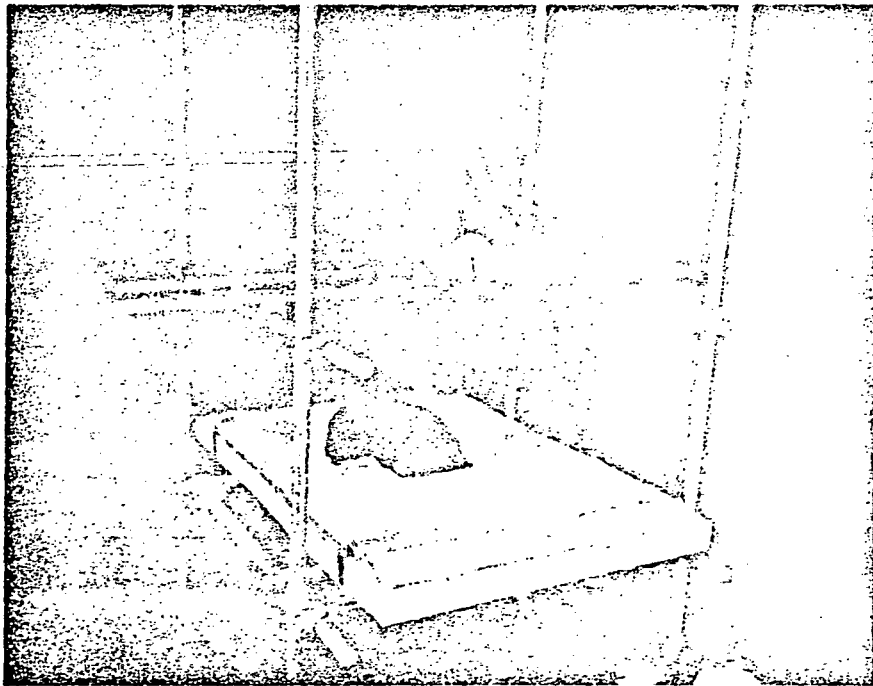


Figure 2. Quartz Lamp Heating Apparatus (Exposed Specimen)

A number of comparative tests were performed to establish whether HAC's quartz lamp test could be used for preliminary qualification. Two major differences between the HAC quartz lamp apparatus and NASA's fuel fired furnace are: (1) the quartz lamp rig produces thermal energy which is virtually 100 percent radiative (NASA fuel furnace is 90 percent radiative), and (2) the heat flux on the coating varies as the coating surface intumesces toward the lamps. Test results, however, indicated that HAC's thermal efficiency ratings were reasonably close to those obtained at Ames on the same lot of coating.

Procedure for quartz lamp thermal efficiency tests. - The heating apparatus shown in Figure 1 consisted of three gold plated Marquardt reflectors each fitted with five General Electric No. 500 T3/CL/HT lamps. With bottom edges of the reflectors positioned approximately 10.2 cm (4 in.) from the test panel, and approximately 200 volts across each of the three banks of lamps, a heat flux of 10 Btu/ft²-sec was achieved. A Hy-Cal Model C-1300-A-60-072 calorimeter (Hy-Cal Engineering Co., Santa Fe Springs, Calif.) was positioned at several places within a 10.2 cm (4 in.) diameter area to check the heat flux, and the voltage was adjusted with a Variac (Type 50-B, 20A, 270V) as required.

An iron-constantan thermocouple was taped to the back of the steel test panel with the thermocouple bulb touching the center insulated disk. A daub of Dow Corning 340 Heat Sink compound was put on and around the thermocouple bulb, and the test panel was then placed into a fitted recess in the asbestos cement board platform. A small flat stainless steel spring with a thin sheet of asbestos paper between it and the thermocouple maintained intimate contact of the thermocouple to the back side of the test panel. Finally a 0.64 cm (1/4 in.) mask of asbestos paper, with a 7.0 cm (2-3/4 in.) square hole, was placed over the test panel.

When the main switch on the Variac was thrown, the drive on the strip chart recorder was started. Sufficient accuracy was obtained by operating the recorder (Moseley Autograph Model 7100B) at 15 cm/min and a full scale deflection of 20 mV. The test was usually terminated when the back side temperature reached 232°C (450°F).

Test specimen preparation. - Test specimens were prepared in accordance with the procedures outlined in Specifications No. A-16839 (B) and (D). Cold rolled steel test panels 1.45 mm (57 mils) thick were degreased, dry abrasive blasted at 7.0 kg/sq. cm (100 psig) with 60 mesh flint abrasive, blown clean of dust and coated within 24 hours.

Part A of the 45B3 coating was redispersed with a low speed laboratory mechanical propeller type stirrer and the required quantity transferred to a mixing container. Correct proportions of Parts B and C were added in turn to Part A and the components thoroughly blended with the stirrer.

The 45B3 coating was spray applied in multiple coats of approximately 127 μ (5 mils) each until the required dry film thickness was achieved. Ten to fifteen minutes was allowed between coats, and the coated specimens were air dried for 10 days (unless otherwise noted) before testing. Spray equipment consisted of a Binks No. 18 pressure pot gun with a 66SD Air Cap, 66SS Fluid Nozzle, operated at a line pressure of 15 - 20 psig (1.0 - 1.4 kg/sq. cm) and a pot pressure of 10 psig (0.7 kg/sq. cm).

The coating required a certain amount of skill to apply properly. Initial attempts resulted in coatings with a very rough appearance and poor cohesive properties. After sufficient experience, however, these difficulties were overcome.

The 313 coating was mixed for application in the same fashion as that described for the 45B3 coating. After parts A, B and C were thoroughly blended, the Refrasil fibers were slowly added under agitation. The low speed mechanical stirring continued for approximately 10 minutes and was followed by a 5 minute high speed mixing.

Spray equipment and application of the 313 coating were similar to the 45B3 coating in respect to multiple coats, drying between coats, 10 day cure, etc.

Because of the Refrasil fibers in the 313 coating, clogging of the spray gun nozzle was a chronic problem and rough coatings were difficult to avoid. Several other spray gun/nozzle combinations and air/fluid pressure combinations were tried before a reasonably satisfactory coating was obtained.

Special test procedures. — Special test procedures utilized were as follows:

- (1) Density was determined by displacement in hexane.
- (2) Taber Abrader test was performed with CS-10 wheels and 500 gram load.
- (3) Flexibility test utilized a 227 g (0.50 lb.) steel ball, 3.81 cm (1.50 in.) diameter, falling from a height of 1.83 m (6 feet). Test Panels were supported, coated face up, on a steel plate having a 1.00 in. (2.54 in.) diameter hemispherical hole. Coating thickness of test panels was 1.02 — 1.06 mm (40 — 42 mils).
- (4) Thermal efficiency tests were performed with quartz heating lamps at 10 Btu/ft²-sec.

Results of qualification tests of 45B3 and 313 coatings. — The results of the qualification tests performed on the various production batches of 45B3 and 313 coatings are presented in Tables XI, XII, XIII, XIV, XV and XVI. These represent production lots number 8-18-71, 11-5-71, 12-8-71, 2-7-72 and 2-23-72.

Figures 3 and 4 show typical specimens that intumesced well during the thermal efficiency test and the linear expansion test. Figure 3 is the picture of thermal efficiency test specimen JJ-12 with 45B3 coating Lot 12-8-71 (thermal efficiency was 94.5 sec/mm or 2.4 sec/mil). Figure 4 shows specimen S-7 with 313 coating Lot 12-8-71 (1.09 mm or 43 mils thick) after exposure to the 350°C (662°F) linear expansion test. Specimen S-7 produced a growth of 150 X measured along the axis and a vertical rise of 127 X.

TABLE XI
 QUALIFICATION TEST RESULTS OF 45B3 COATING
 LOT 8-18-71, YSTRAL MIXED

Test	Spec. A-16839 (B) Requirement	Test Value (1)
Appearance	Brownish yellow, hard, integral film	Brownish yellow, hard, integral film with rough texture.
Tensile Strength	112 ±7 kg/sq. cm (1600 ±100 psi)	Not tested because of brittle film.
Density	1.42 ±0.05 g/cc	1.464 g/cc
Temperature of Intumescence	275 ±10°C	278, 282, 280, 270°C Ave = 278°C
Char Yield	42 ±2 percent	2 percent ⁽²⁾
Abrasion Resistance	205 ±10 mg. loss/1000 cycles	Not tested.
Flexibility	0.18 ±0.014 kg-meters (1.3 ±0.1 foot-pounds)	Not tested.
Linear Expansion	60 x original thickness, minimum	59 X, 48 X Ave. height = 54 X
Thermal Efficiency	Time to reach 204°C (400°F) back side temp ≥ 95 sec.	41 seconds ⁽³⁾ (Char height ≈ 54 cm or 2-1/8 in.) 39 seconds ⁽³⁾ (Char height ≈ 51 cm or 2 in.) Ave. = 40 seconds

¹Coatings were air dried for a minimum of 10 days.

²Outside laboratory experienced difficulty in performing test and result is probably incorrect.

³Thickness of coatings were 0.79 mm (31 mils). Back side temperature approached 400°F before intumescence started. Temperature at 95 sec was 253°C (487°F) and 260°C (500°F) respectively for specimens I-2 and I-10.

TABLE XII
 QUALIFICATION TEST RESULTS OF 45B3 COATING
 LOT 11-5-71, YSTRAL MIXED

Test	Spec. A-16839 (B) Requirement	Test Value (1)
Appearance	Brownish yellow, hard, integral film	Brownish yellow, hard, integral film
Tensile Strength	112 ± 7 kg/sq. cm (1600 ± 100 psi)	1050, 1070, 930, 1020, 1640, 1050, 1290, 1560 psi, Ave. = 85 kg/sq. cm (1201 psi)
Density	1.42 ± 0.05 g/cc	1.47 g/cc
Temperature of Intumescence	275 ± 10°C	280-288, 275-280, 276-285, Ave. = 281°C
Char Yield	42 ± 2 percent	35, 38 Ave. = 36.5 percent
Abrasion Resistance	205 ± 10 mg. loss/1000 cycles	245, 335, 211, 228, 374, 236 ⁽²⁾ Ave. = 271 mg. loss/1000 cycles
Flexibility	0.18 ± 0.014 kg-meters (1.3 ± 0.1 foot-pounds)	No coating fracture at 0.21, 0.28 and 0.41 kg-m (1.5, 2 and 3 ft-lbs)
Linear Expansion	60 X original thickness, minimum	76, 23, 54 ⁽³⁾ Ave. = 51 X original thickness
Linear Expansion after 30 days Humidity	60 X original thickness, minimum	Length = 115X, height = 70X; Length = 119X, height = 92X Ave. length = 117X ⁽⁴⁾ Ave. height = 81X
Thermal Efficiency	78.8 seconds/mm (2.0 seconds/mil) ⁽⁵⁾	55.2 sec/mm (1.40 sec/mil) Char height = 7.7 cm (3 in.) 59.5 sec/mm (1.51 sec/mil) Char height = 10.2 cm (4 in.) Ave. = 57.2 sec/mm or (1.45 sec/mil)

¹ Dry film thickness of coatings was 1.52 - 1.83 mm (60 - 72 mils). Test specimens were air dried 24 hours and then force dried for 16 hours at 66°C (150°F)

² High abrasion weight losses of 335 and 374 mg/1000 cycles were obtained on coatings having a different appearance than the other four tested. Although all six panels were coated during the same sequence, the above two were darker in color with scattered spots of lighter color.

³ Sample H-2 (coating thickness 1.40 mm or 0.055 in.) which produced a large volume of char and a linear expansion of 76X was placed in a preheated 350°C oven on a preheated sheet of asbestos. Edges of test panel were not painted. Intumescence started in 5 minutes and proceeded uniformly.

Sample H-4 (coating thickness 1.60 mm or 0.063 in.) which provided a 23X linear expansion was placed on a cold sheet of asbestos and then put into the preheated oven. Edges of the test panel had been primed (TT-P-664) approximately three days before testing. Intumescence started in approximately 15 minutes. Edges of sample intumescenced slightly compared to center.

Sample H-7 (coating thickness 1.40 mm or 0.055 in.) which produced a large volume of char and a linear expansion of 54 times was placed in a preheated oven on a preheated sheet of asbestos. Paint on edges was partially removed by wiping with solvent prior to the test. Intumescence started after 5 minutes but did not proceed uniformly; that is, one edge intumescenced very slightly.

⁴ Length along the axis of the char, in addition to height above the base, is given because the char leaned over during intumescence.

⁵ Thermal efficiency requirements of specification were changed by Technical Monitor to 2.0 seconds/mil on NASA's fuel fired furnace.

⁶ Intumescence did not commence until approximately 80 seconds (i.e., back side temperature of ~375°F). Thermal efficiency of 1.40 was for specimen 1-2, coating thickness 1.70 mm (67 mils). Thermal efficiency of 1.51 was for specimen 1-4, coating thickness 1.75 mm (69 mils).

TABLE XIII
 QUALIFICATION TEST RESULTS OF 45B3 COATING
 LOT 12-8-71, BALL MILLED

Test	Spec. A-16839 (B) Requirement	Test Value (1)
Appearance	Brownish yellow, hard, integral film	Brownish yellow, hard, integral film
Tensile Strength	112 ± 7 kg/sq. cm (1600 ± 100 psi)	130 kg/sq. cm (1760, 1950 Ave. = 1855 psi) ⁽²⁾
Density	1.42 ± 0.05 g/cc	1.46 g/cc
Temperature of Intumescence	275 ± 10°C	265 - 280°C
Char Yield	42 ± 2 percent	46.5 percent
Abrasion Resistance	205 ± 10 mg. loss/1000 cycles	146, 142, 145, 149 Ave. = 145 mg/1000 cycles
Flexibility	0.18 ± 0.014 kg-meters (1.3 ± 0.1 foot-pounds)	No coating fracture at 0.28 and 0.41 kg-m (2 and 3 ft-lbs) direct or reverse. ⁽³⁾
Linear Expansion	60 X original thickness, minimum	Length 149X, height 89X; Length 134X, height 105X Ave. length = 142X ⁽⁴⁾ Ave. height = 97X ⁽⁴⁾
Linear Expansion after 30 days Humidity	60 X original thickness, minimum	Length = 109X, height = 84X; Length = 103X, height = 87X Ave. length = 106X ⁽⁴⁾ Ave. height = 86X ⁽⁴⁾
Thermal Efficiency	78.8 seconds/mm (2.0 seconds/mil) ⁽⁵⁾	93.8 sec/mm (2.38 sec/mil) (6) Char length = 17.1 cm (6-3/4 in.) 88.2 sec/mm (2.26 sec/mil) Char length = 14.6 cm (5-3/4 in.) Ave. = 91.5 sec/mm (2.32 sec/mil)

¹ Dry film thickness of coatings was 0.99 - 1.32 mm (39 - 52 mils) except for thermal efficiency tests which was 2.06 - 2.21 mm (81 - 87 mils). All test panels were air dried for 10 day minimum before testing.

² Two specimens failed at less than 200 psi due to incorrect test procedure.

³ Coating thickness was 1.04 - 1.29 mm (41 - 51 mils). Coating was face down for reverse impact.

⁴ Specimens were placed in a preheated 350°C oven on a preheated sheet of asbestos-cement board. Since the char had leaned over, the distance from the center of the panel along the axis of the char was used to calculate the linear expansion. The linear expansion representing the height perpendicular to the panel was also reported.

⁵ Thermal efficiency requirements of the specification were changed by Technical Monitor to 2.0 seconds/mil on NASA's fuel fired furnace.

⁶ Thermal efficiency of 2.38 was for specimen JJ-9, coating thickness 2.14 mm (84 mils). Thermal efficiency of 2.26 was for specimen JJ-5, coating thickness 1.78 mm (70 mils). If coating thickness (which was measured with a micrometer) is adjusted to compensate for roughness (i. e., 5 mils for JJ-9 and JJ-5), the thermal efficiency values would be 2.53 and 2.40 seconds/mil respectively. Because of the horizontal direction of the char, length rather than height above the panel is reported.

TABLE XIV
 QUALIFICATION TEST RESULTS OF 313 COATING
 LOT 12-8-71, BALL MILLED⁽¹⁾

Test	Spec. A-16839 (D) Requirement	Test Value (2)
Appearance	Brownish yellow, hard, integral film	Brownish yellow, hard, integral film, rough texture
Tensile Strength	126 ± 14 kg/sq. cm (1800 ± 200 psi)	897, 1860, 1580, 2520 psi Ave. = 120 kg/sq. cm (1714 psi)
Density	1.50 ± 0.05 g/cc	1.43 g/cc
Temperature of Intumescence	285 ± 15°C	250 - 275°C
Char Yield	46 ± 3 percent	51.0 percent
Abrasion Resistance	100 ± 20 mg. loss/1000 cycles	157, 157 Ave. = 157 mg/1000 cycles
Flexibility	0.18 ± 0.014 kg-meters (1.3 ± 0.1 foot-pounds)	No coating fracture at 0.21, 0.28 and 0.41 kg-m (1, 2 and 3 ft-lbs) ⁽³⁾
Linear Expansion	60 X original thickness, minimum	Length = 150X, height = 127X; Length = 178X, height = 142X Ave. length = 164X ⁽⁴⁾ Ave. height = 134X ⁽⁴⁾
Linear Expansion after 30 days Humidity	60 X original thickness, minimum	Length = 119X, height = 93X; Length = 116X, height = 95X Ave. length = 118X ⁽⁴⁾ Ave. height = 94X ⁽⁴⁾
Thermal Efficiency	78.8 seconds/mm (2.0 seconds/mil) ⁽⁵⁾	98.5 sec/mm (2.50 sec/mil) Char length = 6.3 cm (2-1/2 in.) 91.0 sec/mm (2.31 sec/mil) Char length = 5.7 cm (2-1/4 in.) Ave. = 94.5 sec/mm (2.40 sec/mil) ⁽⁶⁾

¹ Part A of formula was prepared by ball milling polysulfide resin, salt and MEK. Refrasil was stirred in afterward.

² Dry film thickness of coatings was 0.84 - 0.99 mm (33 - 39 mils) except for thermal efficiency and flexibility tests. All panels were air dried for 10 days minimum before testing.

³ Coating thickness was 0.96 - 1.19 mm (38 - 47 mils).

⁴ Specimens S7 and S8 were placed in a preheated 350°C oven on a preheated sheet of asbestos-cement board. Since the char had leaned over, the distance from the center of the panel along the axis of the char was used to calculate the linear expansion. The "vertical" linear expansion, also reported, represents the height perpendicular to the panel.

⁵ Thermal efficiency requirements of the specification were changed by Technical Monitor to 2.0 seconds/mil on NASA's fuel fired furnace.

⁶ Thermal efficiency values obtained for specimens T5 and T6 were 2.50 and 2.31 respectively. Specimen T5 machined to a smooth finish of 77 mils while specimen T6 was left in the rough as-sprayed condition. If the micrometer measured thickness of 95 mils for specimen T6 is reduced to 85 mils to compensate for roughness, the Thermal Efficiency would be 2.58 rather than 2.31 sec/mil. Because of the horizontal direction of the char, length rather than height above the panel is reported.

TABLE XV
 QUALIFICATION TEST RESULTS OF 45B3 COATING
 LOT 2-07-72, BALL MILLED

Test	Spec. A-16839 (B) Requirement	Test Value (1)
Appearance	Brownish yellow, hard, integral film	Brownish yellow, hard, integral film
Tensile Strength	112 ± 7 kg/sq. cm (1600 ± 100 psi)	1180, 2030, 860, 2230, 1710, 2000 Ave. = 117 kg/sq. cm (1665 psi)
Density	1.42 ± 0.05 g/cc	1.47 and 1.48 Ave. = 1.475 g/cc
Temperature of Intumescence	275 ± 10°C	244 - 250°C
Char Yield	42 ± 2 percent	44 percent
Abrasion Resistance	205 ± 10 mg. loss/1000 cycles	158, 150, 141, and 152 Ave. = 150 mg/1000 cycles
Flexibility	0.18 ± 0.014 kg-meters (1.3 ± 0.1 foot-pounds)	No coating fracture or chipping at 0.414 kg-meters (3 foot-pounds)
Linear Expansion	60 X original thickness, minimum	Height = 108X and 105X Ave. = 107X ⁽²⁾
Linear Expansion after 30 days Humidity	60 X original thickness, minimum	Not tested
Thermal Efficiency	78.8 seconds/mm (2.0 seconds/mil) ⁽³⁾	83.5 sec/mm (2.12 sec/mil) Char length ≈ 25 cm (10 in.) 90.5 sec/mm (2.30 sec/mil) Char length 25 cm (10 in.) Ave. = 87.0 sec/mm (2.21 sec/mil) ⁽⁴⁾

¹ Dry film thickness of coating was 0.94 - 1.18 mm (37 - 45 mils) except for thermal efficiency tests which was 2.02 - 2.16 mm (79 - 85 mils). All test panels were air dried a minimum of 10 days before testing.

² Specimens were placed in a preheated 350°C oven on a preheated sheet of asbestos-cement board.

³ Thermal efficiency requirement of specification was changed by Technical Monitor to 2.0 sec/mil on NASA's fuel fired furnace.

⁴ Thermal efficiency of 2.12 was for specimen IE-1, coating thickness 2.16 mm (85 mils). Thermal efficiency of 2.30 was for specimen IE-4, coating thickness 2.01 mm (79 mils). Because of horizontal nature of the char, length rather than height above the panel is reported.

TABLE XVI
 QUALIFICATION TEST RESULTS OF 45B3 COATING
 LOT 2-23-72, BALL MILLED

Test	Spec. A-16839 (B) Requirement	Test Value (1)
Appearance	Brownish yellow, hard, integral film	Brownish yellow, hard, integral film
Tensile Strength	112 ± 7 kg/sq. cm (1600 ± 100 psi)	895, 1510, 1350 Ave. = 88 kg/sq. cm (1251 psi) ⁽²⁾
Density	1.42 ± 0.05 g/cc	1.45 g/cc
Temperature of Intumescence	275 ± 10°C	238 - 248°C
Char Yield	42 ± 2 percent	47.5 percent
Abrasion Resistance	205 ± 10 mg. loss/1000 cycles	136, 130, 128 and 126 Ave. = 130 mg/1000 cycles
Flexibility	0.18 ± 0.014 kg-meters (1.3 ± 0.1 foot-pounds)	No coating fracture or chipping at 0.414 kg/m (3 ft-lbs)
Linear Expansion	60 X original thickness, minimum	Height = 97X and 90X Ave. = 94X ⁽³⁾
Linear Expansion after 30 days Humidity	60 X original thickness, minimum	Not tested
Thermal Efficiency	78.8 seconds/mm ⁽⁴⁾ (2.0 seconds/mil)	95.0 sec/mm (2.41 sec/mil) Char length ≈ 25 cm (10 in.) 89.9 sec/mm (2.28 sec/mil) Char length ≈ 25 cm (10 in.) Ave. = 92.2 sec/mm ⁽⁵⁾ (2.34 sec/mil)

¹ Dry film thickness of coating was 0.94 - 1.22 mm (37 - 48 mils) except for thermal efficiency tests which was 2.38 - 2.56 mm (94 - 101 mils). All test panels were air dried a minimum of 10 days before testing.

² Three specimens failed below 35 kg/sq. cm (500 psi) due to chipped edges.

³ Specimens were placed in a preheated 350°F oven on a preheated sheet of asbestos-cement board.

⁴ Thermal efficiency requirements of specification was changed by Technical Monitor to 2.0 sec/mil on NASA's fuel fired furnace.

⁵ Thermal efficiency of 2.41 was for specimen IVE-2, coating thickness 2.38 mm (94 mils). Thermal efficiency of 2.28 was for specimen IVE-4, coating thickness 2.38 mm (94 mils). Because of horizontal nature of the char, length rather than height is reported.

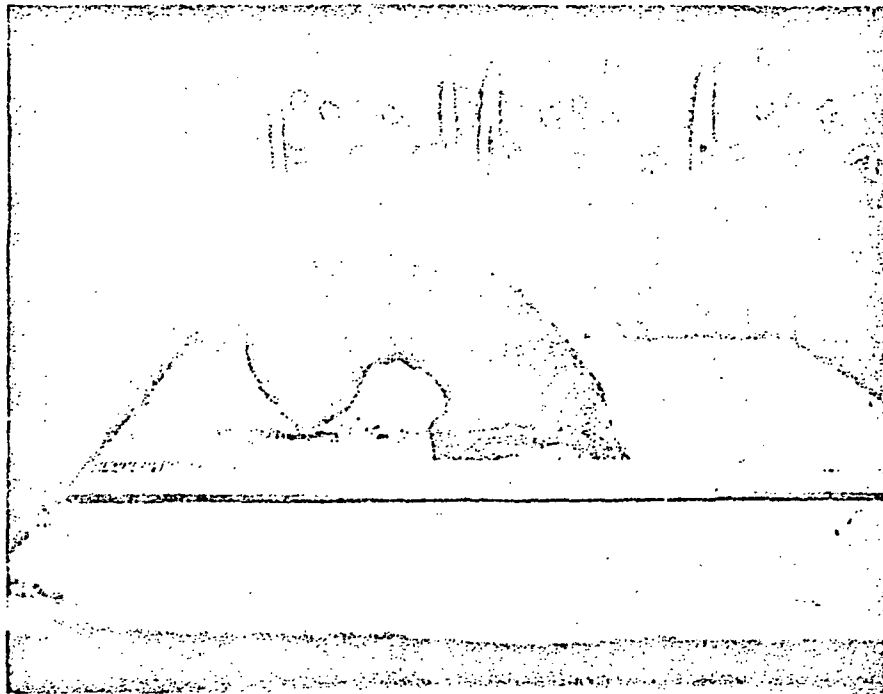


Figure 3. Specimen JJ-12, 45B3 Coating,
Lot 12-8-71, After Quartz Lamp Thermal
Efficiency Test (T. E. = 94.5 sec/mm or
2.4 sec/mil)

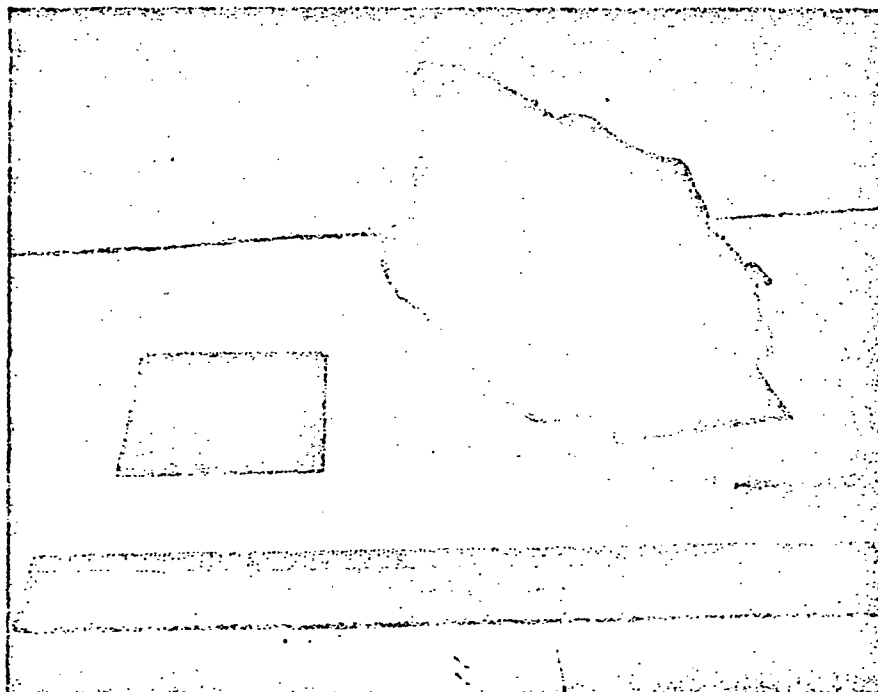


Figure 4. Unexposed Specimen and Specimen S-7,
313 Coating Lot 12-8-71 (L. E. = 150X
Along Axis and 127X Vertical Direction)
After Linear Expansion Test.

Comparison of Thermal Efficiency Test Results

Results of the quartz lamp thermal efficiency tests performed at HAC have been extracted from the Qualification Test data (Tables XI-XVI) and are presented in Tables XVII-XXIV. Where available these data are compared with results obtained by Ames on their fuel fired furnace. In addition, performance of several experimental batches tested during the investigation of the package stability problems have been included. Unless otherwise specified, thermal efficiency tests were conducted at a heat flux of 10 Btu/ft²-sec.

Package Stability of Coating

Observation of problem. - As previously described, three adverse conditions were observed in Part A (i.e., intumescent salt, polysulfide resin, MEK mixture).

Black deposit: Even though the tin pails used for packaging Part A were lined with a Heresite phenolic varnish, a reaction took place with the can. In the several weeks of storage, a loose black deposit formed on the wall of the container where it was in contact with the supernatant liquid (i.e., the LP-3 polysulfide and MEK).

Formula 313 Part A Lot 8-18-71 left over from the original manufacture had been stored in unlined tin coated can. This can had a large quantity of loose black deposit on the wall in contact with the supernatant liquid, and slight agitation caused the liquid to turn black. Spectrographic analysis of the black deposit showed iron and tin as the major elements, presumed as the sulfide.

Gelation: Gelation of 45B3, Lot 8-18-71, Part A was observed in a pail that had been opened several times to remove a portion for test work. Each time the contents were vigorously agitated with a motor driven propeller blade type stirrer. Undoubtedly, air was entrained in the material during each mixing. Three days after the last mixing of this 45B3 Part A, it was found to be gelled. This occurred six weeks after manufacture. It should be noted that Part A originally occupied approximately 0.4 of the volume of the two gallon pail and only about 0.2 at the time of gelation. 45B3 coatings applied from this container three days before gelation was observed did not intumesce during quartz lamp tests.

At this point, it became obvious that 45B3 Part A containing the intumescent salt, LP-3 and MEK was undergoing a reaction in the can. As an interim measure, the Furane Company was instructed to immediately remove Part A of the 45B3 formula and also Part A of the 313 formula from the metal containers and package them in 5 gallon polypropylene pails. Ullage was swept out with dry nitrogen before sealing the lids.

Hard settling of 313 Part A: When the above transfer operation was conducted at the Furane Plastics Co., it was discovered that Part A of 313 coating, Lot 9-02-72, containing the Refrasil fibers had settled out extremely hard. In less than a month from the date of manufacture, the 313 Part A had reached a

TABLE XVII

COMPARISON OF THERMAL EFFICIENCY VALUES FOR THIN FILMS
OF 45B3 COATING, LOT 8-18-71, YSTRAL MIXED

Specimen ⁽¹⁾ Description	Cure Method	Test Method	Thermal ⁽²⁾ Efficiency	Remarks
I-5 (1331-07) 0.79 mm (31 mils)	Air dried 10+ days at RT	Quartz lamps ⁽³⁾ at Hughes	1.25 sec/mil (49.5 sec/mm)	Back side approached 400°F (204°C) before intumescence started. Firm soft char ~ 2-1/8 in. Temp. at 95 sec was 288°C (550°F)
I-2 (1331-07) 0.79 mm (31 mils) ²	Air dried 10+ days at RT	Quartz lamps at Hughes	1.32 sec/mil (54.8 sec/mm)	Same as I-5 except temp. at 95 sec was 253°C (487°F)
I-10 (1331-07) 0.79 mm (31 mils)	Air dried 10+ days at RT	Quartz lamps at Hughes	1.25 sec/mil (49.5 sec/mm)	Same as I-5 except temp. at 95 sec was 260°C (500°F)
(1331-07) 0.79 mm (31 mils)	Air dried 10+ days at RT	Fuel furnace at Ames	1.1 sec/mil (43 sec/mm)	Thermal efficiency was reported to be the same for thin (> 30 mil) coatings made at Ames

¹Part A of 45B3 coating manufactured 8-18-71 was packaged in 2 gal (7.6 liter) Heresite coated tin pails less than half full. Coating applied 8-28-71 was cured and then sanded down to the required 0.76-0.81 mm (30-32 mils). Thickness was measured on the insulated disk at center of test panel.

²Thermal efficiency equals time for back side to reach 204°C (400°F) divided by the thickness of the coating.

³Specimen I-5 was tested with quartz lamps at a heat flux of 12 Btu/ft²-sec. All other specimens were tested at a heat flux of 10 Btu/ft²-sec.

TABLE XVIII

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3
COATINGS MANUFACTURED BY DIFFERENT METHODS

Specimen Description	Coating Thickness (1)	Cure Method (2)	Thermal Efficiency (3)	Remarks
1A. Ystral ⁽⁴⁾ mixed Lot 8-18-71	1.14 mm (45 mils)	16 hrs at 66°C (150°F)	38.6 sec/mm (0.98 sec/mil)	No intumescence, hard char ~0.32 cm (1/8 in.)
1C. Ystral ⁽⁴⁾ mixed Lot 8-18-71 base plus fresh top coat (~15 mils) ⁽⁵⁾	1.52 mm (60 mils)	16 hrs at ⁽⁵⁾ 66°C. (150°F)	61.8 sec/mm (1.57 sec/mil)	Top portion intumesced for 5-10 sec. - bottom slightly. Started at ~18 sec. Char ~3.8 cm (1-1/2 in.), top fragile.
3A. Ystral ⁽⁴⁾ mixed Lot, 8-18-71 Part A ball milled 2 hrs	1.37 mm (54 mils)	16 hrs at 66°C (150°F)	37.9 sec/mm (0.96 sec/mil)	No intumescence, hard char ~0.32 cm (1/8 in.)
4A. New 45B3 Part A ball ⁽⁶⁾ milled 4 hrs	1.55 mm (61 mils)	16 hrs at 66°C (150°F)	81.5 sec/mm (2.06 sec/mil)	Excellent intumescence. Started at ~15 sec. Very fragile char ~3 in. (7.6 cm). Lifted off right side at end of test period but ~1/16 in. (0.16 cm) of char on metal.
4B. New 45B3 Part A ball ⁽⁶⁾ milled 4 hrs	1.57 mm (62 mils)	16 hrs at 66°C (150°F)	78.8 sec/mm (2.00 sec/mil)	Excellent intumescence. Started at ~13 sec. Very fragile char ~3 in. (7.6 cm)

TABLE XVIII Continued

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3 COATINGS MANUFACTURED BY DIFFERENT METHODS

Specimen Description	Coating (1) Thickness	Cure (2) Method	Thermal (3) Efficiency	Remarks
4C. New 45B3 Part A ball milled 4 hrs (6)	1.68 mm (66 mils)	16 hrs at 66°C (150°F)	118 sec/mm (3.0 sec/mil)	Thermal efficiency test performed on Ames' fuel furnace.
EX - 45B3 NASA Ames prepared coating and specimen	0.89 mm (35 mils)	Air dried 10+ days at RT	94.5 sec/mm (2.40 sec/mil)	Good intumescence. Started at ~ 17 seconds. Very fragile char ~ 2-1/4 in. (5.7 cm)

¹ Thickness was measured on the insulated disk at the center of the test panel.

² Coatings on test specimens (except 1C and EX-45B3 NASA) were air dried for three days at room temperature before baking at 150°F.

³ Thermal efficiency test was conducted with quartz lamps at Hughes except for specimen 4C which was tested at Ames. Heat flux was 10 Btu/ft²-sec. Thermal efficiency equals time of back side to reach 400°F (204°C) divided by thickness of the coating.

⁴ Part A material was taken from the same can previously opened several times and was less than 1/3 full. The coating was applied on 9-24-71 and Part A was found to have jelled when inspected 9-27-71.

⁵ Approximately 45 mils (1.14 mm) of 45B3 Lot 8-18-71 (same as specimen 1A) dried 2-1/2 days and was given an ~15 mil topcoat. The topcoat was prepared by blending Stud-milled salt, LP-3 resin and MEK with a high speed laboratory stirrer. After drying the topcoat for several hours the test panel was cured at 150°F for 16 hours.

⁶ Specimens 4A, 4B and 4C were prepared by ball milling "as received" salt, LP-3 resin and MEK for 4 hours and rinsing mill with additional MEK.

TABLE XIX
COMPARISON OF THERMAL EFFICIENCY VALUES FOR THICK FILMS
OF 45B3 COATING, LOT 8-18-71, YSTRAL MIXED

Specimen Description (1)	Coating Thickness (2)	Test Method (3)	Thermal Efficiency (4)	Remarks
5 (G1331-13)	1.50 mm (59 mils)	Quartz lamps at Hughes	49.5 sec/mm (1.25 sec/mil)	Intumescence started at ~14 sec but was of short duration. Firm, fairly hard char ~1-1/8 in. (2.9 cm)
6 (G1331-13)	1.50 mm (59 mils)	Quartz lamps at Hughes	54.8 sec/mm (1.39 sec/mil)	Same as specimen 5 except char ~1-1/2 in. (3.8 cm)
1, 2, 3 and 8 (G1331-13)	1.60-1.70 mm (63-67 mils)	Fuel furnace at Ames	59-67 sec/mm (1.5-1.7 sec/mil)	

¹ Test specimens were prepared on 9-29-71 using a fresh (unopened) can of 45B3 Part A, Lot 8-18-71. Part A was packaged on 8-18-71 in Heresite coated 2 gal. tin pails and were less than one half full. Coatings were applied, dried 22 hours at room temperature, plus 4 hours at 100°F (38°C) plus 4 hours at 125°F (52°C) plus 16 hours at 150°F (66°C).

² Thickness of coating was measured on the insulated disk at the center of the panel.

³ Heat flux was 10 Btu/ft²-sec.

⁴ Thermal efficiency equals time for back side of steel panel to reach 400°F (204°C) divided by the thickness of the coating.

TABLE XX

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3
COATING, LOT 11-5-71, YSTRAL MIXED

Specimen Description (1)	Cure (2)	Test Method (3)	Thermal Efficiency (4)	Remarks
I-2 1.75 mm (69 mils)	16 hours at 66°C (150°F)	Quartz lamps at Hughes	55.2 sec/mm (1.40 sec/mil)	Intumescence started late. Time to reach 232°C (450°F) was 168 sec
I-4 1.70 mm (67 mils)	16 hours at 66°C (150°F)	Quartz lamps at Hughes	59.5 sec/mm (1.51 sec/mil)	Intumescence started late at ~80 sec. and back side temp ~191°C (375°F). Time to reach 232°C (450°F) was 158 sec
I-1 1.65 mm (65 mils)	16 hours at 66°C (150°F)	Fuel furnace at Ames	58.6 sec/mm (1.49 sec/mil)	Intumescence started late at 177°C (350°F) back side temp
I-6 1.70 mm (67 mils)	16 hours at 66°C (150°F)	Fuel furnace at Ames	69.7 sec/mm (1.77 sec/mil)	Intumescence started late at 177°C (350°F) back side temp
I-5 1.78 mm (70 mils)	16 hours at 66°C (150°F)	Fuel furnace at Ames	70.9 sec/mm (1.80 sec/mil)	Intumescence started late at 177°C (350°F) back side temp
I-7 1.68 mm (66 mils)	16 hours at 66°C (150°F)	Fuel furnace at Ames	49.2 sec/min (1.25 sec/mil)	Intumescence started late at 177°C (350°F) back side temp

TABLE XX Continued
 COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3
 COATING, LOT 11-5-71, YSTRAL MIXED

Specimen Description (1)	Cure (2)	Test Method (3)	Thermal Efficiency (4)	Remarks
I-11 1.78 mm (70 mils)	Air dried 10+ days at RT	Fuel furnace at Ames	76.8 sec/mm (1.95 sec/mil)	Intumescence started sooner than baked specimens
I-12 1.85 mm (73 mils)	Air dried 10+ days at RT	Fuel furnace at Ames	65.0 sec/mm (1.65 sec/mil)	Char separated from panel at latter stages of test

¹Part A of 45B3 coating Lot 11-5-71 was packaged in full 0.95 liter (1 qt) glass jars with the small ullage swept out with dry nitrogen. Coating thickness was measured on insulated disk at center of test panel.

²Coatings were air dried for 24 hours before 66°C (150°F) cure.

³Heat flux was 10 Btu/ft²-sec

⁴Thermal efficiency equal time for back side temperature of steel panel to reach 204°C (400°F) divided by the coating thickness.

TABLE XXI

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3,
COATING, LOT 12-8-71, BALL MILLED

Specimen Description (1)	Cure	Test Method (2)	Thermal Efficiency (3)	Remarks
JJ-12 2.13 mm (84 mills)	24 hrs at RT plus 16 hrs at 150°F	Quartz lamp at Hughes	93.0 sec/mm (2.36 sec/mil)	Intumescence started at ~ 14 sec Char 13.5 cm (5-1/2 in.)
JJ-11 2.13 mm (84 mills)	24 hrs at RT plus 16 hrs at 150°F	Quartz lamp at Hughes	92.1 sec/mm (2.34 sec/mil)	Intumescence started at ~ 12 sec and increased in vigor at 72 sec. Touched lamps at 11.3 cm (4-7/16 in.) and top burned away at 98 sec. Char 14.6 cm (5-3/4 in.)
JJ-9 2.13 mm (84 mills)	10+ days at RT	Quartz lamp at Hughes	92.1 sec/mm ⁽⁴⁾ (2.38 sec/mil)	Intumescence started at ~ 13 sec and increased in vigor at 76 sec. Char 17.1 cm (6-3/4 in.)
JJ-5 2.08 mm (82 mills)	10+ days at RT	Quartz lamp at Hughes	89.0 sec/mm ⁽⁴⁾ (2.26 sec/mil)	Intumescence started at ~ 14 sec and increased in vigor at 76 sec. Char 14.6 cm (5-3/4 in.)
JJ-3 2.11 mm (83 mills)	4 days at RT plus 13 days at 90% RH, 100°F	Fuel furnace at Ames	86.6 sec/mm (2.2 sec/mil)	

TABLE XXI Continued

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3,
COATING, LOT 12-8-71, BALL MILLED

Specimen Description (1)	Cure	Test Method (2)	Thermal Efficiency (3)	Remarks
JJ-4 2.08 mm (82 mils)	17 days at RT	Fuel furnace at Ames	94.5 sec/mm (2.4 sec/mil)	
JJ-6 2.11 mm (83 mils)	17 days at RT	Fuel furnace at Ames	63.0 sec/mm (1.6 sec/mil)	Severe fissures developed in center of char
SP-1 2.06 mm (81 mils)	24 hrs at RT plus 16 hrs at 150°F plus 15 days at RT	Fuel furnace at Ames	94.5 sec/mm (2.4 sec/mil)	
SP-2 2.08 mm (82 mils)	24 hrs at RT plus 16 hrs at 150°F plus 15 days at RT	Fuel furnace at Ames	106.3 sec/mm (2.7 sec/mil)	
SP-3 2.13 mm (84 mils)	24 hrs at RT plus 16 hrs at 150°F plus 2 days at RT plus 13 days at 90% RH, 100°F	Fuel furnace at Ames	94.5 sec/mm (2.4 sec/mil)	

TABLE XXI Concluded

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3,
COATING, LOT 12-8-71, BALL MILLED

Specimen Description (1)	Cure	Test Method (2)	Thermal Efficiency (3)	Remarks
SP-4 2.11 mm (83 mils)	24 hrs at RT plus 16 hrs at 150°F plus 2 days at RT plus 13 days at 90% RH, 100°F	Fuel furnace at Ames	78.8 sec/mm (2.0 sec/mil)	

¹Part A packaged in glass jars. Coating thickness was measured on insulated disk at center of steel test panel.

²Heat flux was 10 Btu/ft²-sec.

³Thermal efficiency equals time for back side temperature of steel panel to reach 204°C (400°F) divided by the thickness of the coating.

⁴The roughness of the coating was determined to be 10-12 mils based on sanding one corner until smooth. If half of the amount (i.e., 5 mils) is deducted from measured coating thickness, thermal efficiency values for specimens JJ-9 and JJ-5 would be respectively 2.53 and 2.40 (instead of 2.38 and 2.26) sec/mil.

TABLE XXII

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 313
COATING, LOT 12-8-71, BALL MILLED

Specimen Description (1)	Cure	Test Method (2)	Thermal Efficiency (3)	Remarks
T-5 1.95 mm (77 mils) ⁽⁴⁾	12 days at RT	Quartz lamps at Hughes	2.50 sec/mil (98.5 sec/mm)	Intumescence started at ~27 sec. Char 5.7 cm (2-1/4 in.)
T-6 2.41 mm (95 mils)	12 days at RT	Quartz lamps at Hughes	2.31 sec/mil ⁽⁴⁾ (91.2 sec/mm)	Intumescence started at ~16 sec. Char 5.7 cm (2-1/4 in.)
T-1 2.52 mm (99 mils)	7 days at RT plus 13 days at 90% RH, 100°F	Fuel furnace at Ames	2.2 sec/mil (86.6 sec/mm)	
T-3 2.49 mm (98 mils)	20 days at RT	Fuel furnace at Ames	2.0 sec/mil (78.8 sec/mm)	
T-8/ 2.49 mm (98 mils)	20 days at RT	Fuel furnace at Ames	2.2 sec/mil (86.6 sec/mm)	

¹Part A (without refrasil) packaged in glass jars. Coating thickness was measured on the insulated disk at center of steel test panel. Specimen T-5 showed a roughness of 20-30 mils on viewing the edges of the panel with a 7X optical comparator and by using a radiused needle probe on a dial micrometer. T-5 was machined smooth with a fly cutter to 77 mils.

²Heat flux was 10 Btu/ft²-sec.

³Thermal efficiency equals time for back side temperature of steel panel to reach 204°C (400°F) divided by the thickness of the coating.

⁴If thickness of coating is reduced 10 mils (i.e., half of the 20 mil roughness); the thermal efficiency would be 2.58 sec/mil rather than 2.31.

TABLE XXIII

COMPARISON OF THERMAL EFFICIENCY VALUES, 45B3
COATING, LOT 2-07-72, BALL MILLED

Specimen Description (1)	Test Method (2)	Thermal Efficiency (3)	Remarks
IE-1 2.16 mm (85 mils)	Quartz lamps at Hughes	83.5 sec/mm (2.12 sec/mil)	Intumescence started at ~13 sec and increased in vigor at 64 sec. Char ~10 in. long (i.e., along the arc)
IE-4 2.02 mm (79 mils)	Quartz lamp at Hughes	90.5 sec/mm (2.30 sec/mil)	Intumescence started at ~14 sec and increased in vigor at 66 sec. Char ~10 in. long (i.e., along the arc)
IE-2 2.22 mm (87 mils)	Fuel furnace at Ames	--	Char fell off panel
IE-4 2.15 mm (83 mils)	Fuel furnace at Ames	82 sec/mm (2.1 sec/mil)	--
IE-3 1.93 mm (76 mils)	Fuel furnace at Ames	134 sec/mm (3.4 sec/mil)	Specimen holding fixture modified to reduce flame leakage around edges. Greater metal mass acted as heat sink and resulted in higher T.E. value.

TABLE XXIII Concluded
 COMPARISON OF THERMAL EFFICIENCY VALUES, 45B3
 COATING, LOT 2-07-72, BALL MILLED

Specimen Description (1)	Test Method (2)	Thermal Efficiency (3)	Remarks
IE-3 2.16 mm (85 mils)	Fuel furnace at Ames	126 sec/mm (3.2 sec/mil)	Specimen holding fixture modified to reduce flame leakage around edges. Greater metal mass acted as heat sink and resulted in higher T.E. value.

¹Part A packaged in glass jars. Coating thickness was measured on the insulated disk at center of steel test panel. All specimens were air dried a minimum of 10 days at room temperature.

²Heat flux was 10 Btu/ft²-sec.

³Thermal efficiency equals time for back side temperature of steel panel to reach 204°C (400°F) divided by thickness of the coating.

TABLE XXIV

COMPARISON OF THERMAL EFFICIENCY VALUES FOR 45B3
COATING, LOT 2-23-72, BALL MILLED

Specimen Description (1)	Test Method (2)	Thermal Efficiency (3)	Remarks
IV E-4 2.39 mm (94 mils)	Quartz lamps at Hughes	89.8 sec/mm (2.28 sec/mil)	Intumescence started at ~13 sec, slowed, then increased again at 108 sec. Char ~25 cm (10 in.) long
IV E-2 2.39 mm (94 mils)	Quartz lamps at Hughes	95.0 sec/mm (2.41 sec/mil)	Same as for specimen IV E-4
III E-2 2.52 mm (99 mils)	Fuel furnace at Ames	90.6 sec/mm (2.3 sec/mil)	
III E-3 2.46 mm (97 mils)	Fuel furnace at Ames	98.5 sec/mm	Char fell off at end of test
III E-4 2.44 mm (96 mils)	Fuel furnace at Ames	98.5 sec/mm (2.5 sec/mil)	

¹ Part A packaged in glass jars. Coating thickness was measured on the insulated disk at the center of the steel test panel. All specimens were air dried (the Hughes tested specimens for 13 days and the Ames tested specimens for approximately 30 days.)

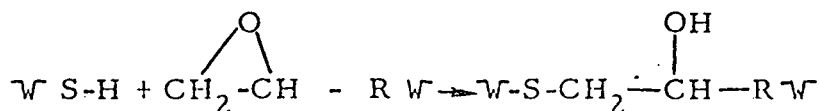
² Heat flux was 10 Btu/ft²-sec.

³ Thermal efficiency equals time for back side temperature of steel panel to reach 204°C (400°F) divided by thickness of the coating.

consistency of tough sod. Proper reincorporation of the settled pigment and Refrasil fibers would have been very difficult.

Chemical reactions contributing to gelation. - Several chemical reactions have been postulated by HAC to explain gelation. These are as follows:

The copolymerization of polysulfides and epoxies proceeds through the base catalyzed addition of the -S-H polysulfide end groups to the epoxy groups. Thus,



The reaction proceeds stoichiometrically until the S-H groups are consumed.

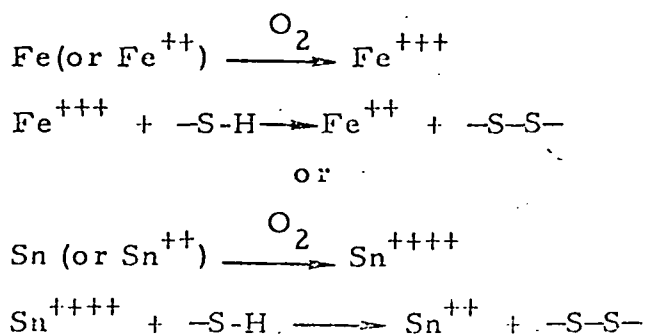
Under suitable oxidative conditions, mercaptan (SH) groups can be readily oxidized to disulfides via a free radical process.



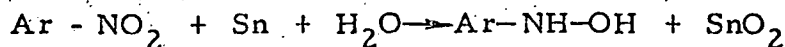
Thus, it is reasonable to expect that this reaction also can occur with polysulfides since they contain on the order of 5 or 6% mercaptan (SH) groups prior to cure. Mild oxidizing agents such as dilute H_2O_2 or CuCl_2 are examples of oxidizers which can promote the coupling.

Having encountered the problem of polymerization (i. e., gelation) in the "A" component of formulat 45B3 one is led to wonder what may have induced the oxidative polymerization and created the apparent shelf life problem.

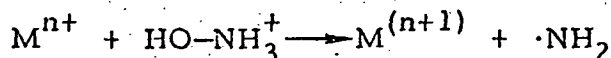
Oxidation by air is of course one of the more reasonable mechanisms and it is highly possible that stannic or ferric ions from the container walls play an important role in catalyzing this reaction or serving as intermediates through which the air oxidation proceeds, thus:



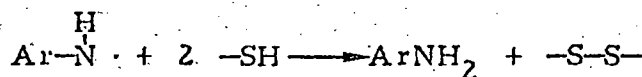
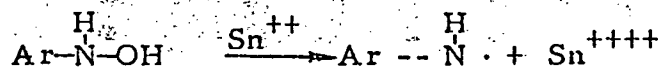
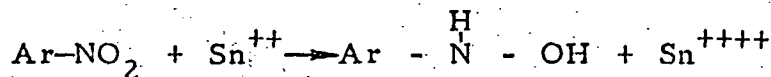
Another mode of oxidation is via the nitro groups of the intumescent salt. For example, the following reaction is feasible with the tin can.



Furthermore, Davis et al, Ref. 7, have shown that hydroxylamines can react with reduced states of metal ions (such as Fe^{++}) to produce $\cdot\text{NH}_2$ free radicals, thus:



The NH_2 radical in this case was substantiated by its ability to polymerize acrylates. By this mechanism it thus should be feasible to oxidize polysulfides with nitrated intumescent salts in the presence of metallic ions, the net reaction being illustrated as follows:



It is quite evident, therefore, that all of the agents necessary to promote either air or nitro group oxidation of the polysulfide are present in the "A" component of formula 45B3. Which reaction mechanism is responsible for the apparent shelf life problem has yet to be verified. However, current evidence seems to indicate that air oxidation initiated the problem. In either case tin, copper or iron contamination seems to be something to avoid."

Mercaptan analysis of Part A from 45B3, Lot 8-18-71 and 313.

Lot 9-02-71. - When the stability problem was first recognized, Part A of production lots of 45B3 (Lot 8-18-71) and 313 (Lot 9-02-71) coatings were transferred from their partially full metal containers to 5 gallon polypropylene pails. Air was purged out with nitrogen before sealing. This transfer was effected on September 30, 1971. On October 15, 1971, samples of the supernatant liquid (i.e., the LP-3 polysulfide dissolved in MEK) were removed and analyzed for mercaptan content (i.e., -S-H). The results of this analysis, performed by Furane Plastics using the Thiokol Product Specification Code LF-241 test method, are reported in Table XXV. The reduction in -S-H content found in the 45B3 and 313 coatings would tend to support the hypothesis for oxidation of the mercaptan groups to disulfide and resultant adverse affect on thermal performance postulated above. "That is, lack of mercaptan causes less copolymerization of the epoxy and polysulfide and greater homopolymerization of the epoxy

resin. The additional cross-linking of the epoxy would reduce thermal plasticity during heating and make for a more rigid and smaller char volume. The net effect, of course, would be to reduce thermal efficiency."

TABLE XXV
MERCAPTAN ANALYSIS

Sample	Description	Wt. Percent -S-H
1	45B3 Lot 8-18-71 (supernatant liquid)	2.91
2	45B3 Lot 8-18-71 (supernatant liquid) duplicate of No. 1	2.78
3	313, Lot 9-2-71 (supernatant liquid)	3.91
4	313, Lot 9-2-71 (supernatant liquid) duplicate of No. 3	3.95
5	LP-3 (previously opened container)*	6.90
6	LP-3, +MEK	7.02
7	LP-3, + salt + MEK (i.e., equivalent to 45B3 with twice as much MEK to promote settling)	
	after 24 hours (Ave. of two)	5.99
	after 48 hours	6.20

*Specification limit is 5.9-7.7%, analysis on 6-24-71 was 6.86%, analysis on 8-25-71 was 6.94% and above analysis of 6.90 was made on 10-15-71.

Flexible Thermal Protection Coating

Manufacture of flexible coating. — At the request of Ames Research Center, three batches of a Flexible Thermal Protection Coating were manufactured. Table XXVI lists the several production lots, along with the method of manufacture and the quantity obtained.

TABLE XXVI

PRODUCTION BATCHES OF FLEXIBLE THERMAL PROTECTION COATING

Lot No.	Quantity Manufactured	Method of Manufacturing	Salt Batch (1)
9-09-71	45.5 l (12 gal)	Ystral mixer ⁽²⁾	7-7-71
9-17-71	37.8 l (10 gal)	Ystral mixer ⁽²⁾	7-7-71
2-10-71	14.0 l (3.7 gal)	Ystral mixer	7-7-71

¹Intumescent salt batches were identified by the date received since they all had the same Allied Chemical Corp. batch number (i.e. No. 0657731). Salt batch 7-7-71 was Stud-milled twice (at Furane Plastics Inc.) to reduce particle size.

²Prechilled MEK and mixing vessel used for manufacture of Part A.

Formula for flexible coating: The formula given in the preliminary specification for the coating, Reference (9), is as follows:

<u>Material</u>	<u>Parts by Weight</u>
<u>Part A</u>	
Polysulfide Polymer, Liquid (LP-3)	18.8
Ammonium salt of 4-nitroaniline-2-sulfonic acid	28.2
Methyl ethyl ketone	13.8
<u>Part B</u>	
Epoxy Resin, Liquid (Epon 828)	9.4
Toluene	3.1
<u>Part C</u>	
Tri (dimethylamino methyl) phenol (DMP-30)	1.9
Toluene	1.9

Material properties of flexible coating. — The material properties measured on the production lots of Flexible Protection Coating are provided in Table XXVII.

TABLE XXVII

MATERIAL PROPERTIES OF PRODUCTION LOTS OF FLEXIBLE THERMAL PROTECTION COATING

Property	Requirement	Lot no. 9-09-71	Lot no. 9-17-71	Lot no. 2-10-71
Part A				
Viscosity ⁽¹⁾	800 — 1200 cps	850 — 880	880	860 — 880
Wt/gal ⁽²⁾	10.4 ± 0.1 lbs/gal 1.25 ± 0.01 g/cc	10.48 lbs/gal 1.26 g/cc	10.50 lbs/gal 1.26 g/cc	10.50 lbs/gal 1.26 g/cc
Fineness of grind	1+	1+	1+	1+
Part B				
Viscosity ⁽¹⁾	80 — 100 cps	80 — 85	86 — 88	85 — 93
Wt/gal ⁽²⁾	8.9 ± 0.1 lbs/gal 1.07 ± 0.01 g/cc	8.95 1.07 g/cc	9.02 1.08 g/cc	8.97 1.08 g/cc
Part C				
Viscosity ⁽¹⁾	10 — 15 cps	15	14 — 15	14
Wt/gal ⁽²⁾	7.6 ± 0.1 lbs/gal 0.91 ± 0.01 g/cc	7.55 0.91 g/cc	7.60 0.91 g/cc	7.59 0.91 g/cc

¹ Measured with a model RTV Brookfield Viscometer with a #2 spindle and a temperature of 20°C (68°F). Part A was at 12 rpm, Part B at 50 rpm and Part C at 100 rpm.

² Wt/gal was measured per Method 4184.1 of Federal Test Method Standard 141A.

Preparation of flexible sheets. - One set of 12 sheets was prepared from Lot 9-09-71 and a second set of 7 sheets was prepared from Lot 2-10-72. The sheets were a minimum of 0.81 mm (32 mils) thick and were 24 X 24 inches (9.45 X 9.45 cm) overall.

First set: The first set of sheets was 0.81 - 0.91 mm (32 - 36 mils) thick. These were manufactured by spraying 4 to 5 box coats, with a 5 to 10 minute air dry between coats, on Mylar film. After 72 hours air drying, the sheets were peeled from the Mylar film and inverted for another 24 hours of air drying. Mylar film was used instead of a mold release to avoid any contamination of the sheets which would interfere with subsequent adhesive bonding. After the three days of cure, the sheets were dry to handle but had a very high contact adhesive property. Portions of the sheets that lightly touched one another could not be separated without tearing the parent material. This contact adhesive property might be usefully employed in affixing the sheets to various surfaces.

Second set: The second set of 7 sheets, 0.81 - 1.12 mm (32 - 44 mils) thick, was prepared in the same manner as the first set. Two of the sheets were fabricated with a reinforcing layer of glass fiber mat to minimize slumping or sagging of the sheets when exposed to a fire. The MIL-Y-1140 glass veil mat varied from 0.14 - 0.22 mm (5.5 - 8.5 mils) with an average thickness of 0.18 mm (7.2 mils). Manufacture of these two reinforced sheets was accomplished as follows:

(1) Sheet 1 (shiny side has uniform color)

(a) Four 90° passes (approximately 12 - 15 mils total) of flexible coating, Lot No. 2-10-72, were applied over the Mylar parting sheet. Each pass was air dried 10 - 15 minutes and the fourth coat was dried 30 - 45 minutes. The mat was laid on the coating and lightly patted down.

(b) Eight additional passes of the flexible coating were applied, 15 - 20 minutes apart, over the mat.

(2) Sheet 2 (shiny side has a few mottled spots)

(a) The first four coats were applied as above but the last coat was allowed to air dry for 1 - 1-1/2 hours. The mat was laid on the coating, a thin Teflon sheet put over it, and the mat imbedded by rolling with a rubber covered roller.

(b) The Teflon sheet was removed and eight additional passes were applied as for sheet 1.

(c) After three days of drying, the Mylar parting sheet was peeled from the flexible sheet. Several void areas (i. e., air pocket formed when the mat was rolled) on the back of the sheet were filled with flexible coating using a "doctor" blade.

All 7 sheets were air dried for three days before removing the Mylar parting sheet. A great deal of difficulty was experienced in removing these 0.13 mm (5 mil) Mylar parting sheets whereas the 0.05 mm (2 mil) sheets used with the first set came off easily. The sheets were then inverted and dried with the bottom face up for an additional four days. Finally, the sheets were inverted

again and dried 4 more days. A test for "blocking" was performed (i.e., samples were laid-up top-to-back and back-to-back under a 2 kg weight for 4 hours). At the end of the test, there was no evidence of the material sticking to itself or of tackiness.

It should be noted that, with some effort, individual flexible sheets could be forced to separate into two layers. Although no definite explanation for this condition is known, it is probably caused by excessive drying between two successive coats resulting from the lunch hour break.

IV. COATING OF HARDWARE

Application of Flexible Protection Coating to Fuel Hose

A 4.4 cm (1-3/4 in.) diameter rubber fuel hose assembly (MIL-H-7061-1-1Q70-06827) approximately 38.1 cm (15 in.) long was coated with 45 mils (1.04 mm) of Flexible Protection Coating. Parts A, B and C were mixed in accordance with the specification, Ref. (9).

The metal fittings were masked, the rubber portion solvent wiped with toluene and the coating applied by spraying. Eight wet coats approximately 5 - 10 minutes apart were applied, an additional eight coats were applied the next day, and the coating was allowed to dry at room temperature for several days. Figure 5 shows the coated hose.

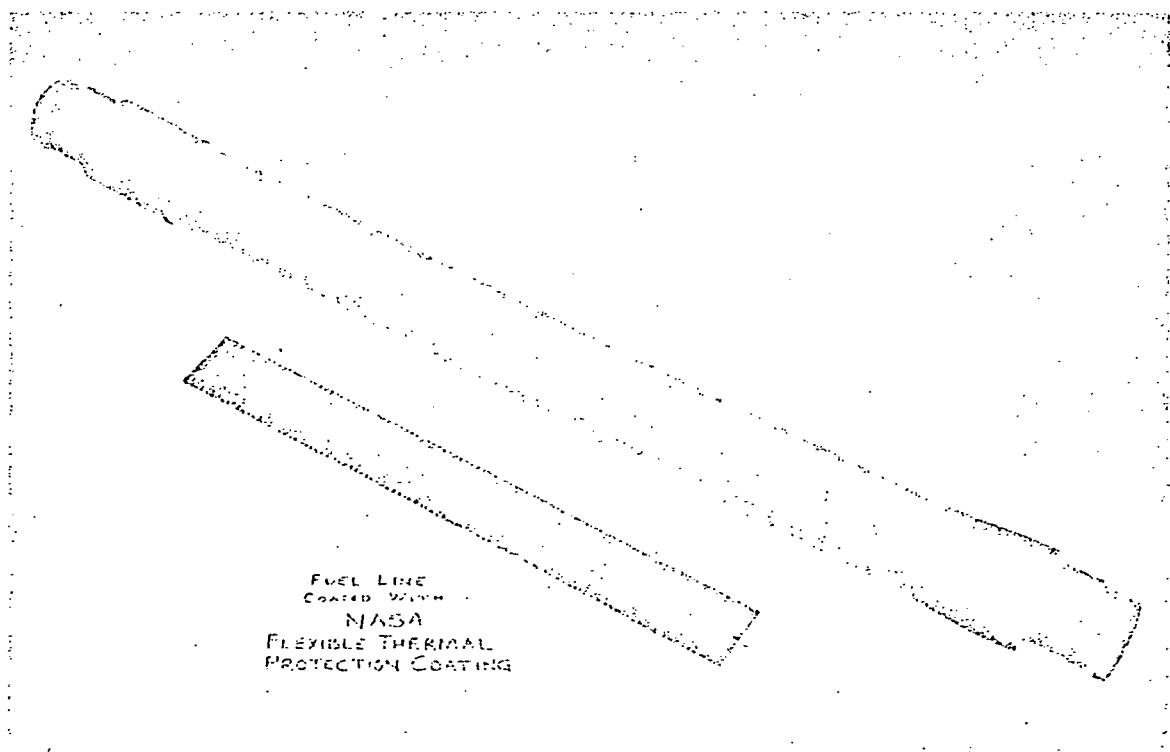


Figure 5. MIL-H-7061-1Q70-06827 Rubber Fuel Hose Coated With Flexible Protection Coating (1.04 mm or 45 mils thick)

Application of 45B3 Thermal Protection Coating to Plywood Panels

Seven exterior grade plywood panels, 0.954 x 30.48 x 30.48 cm (3/8 x 12 x 12 inches) were coated with approximately 1.52 mm (60 mils) of 45B3 coating. 45B3 material from two lots was utilized (i.e., 4 quarts or 3.78 l from Lot 12-8-71 and 1 pint or 0.574 l from Lot 11-5-71 mixed together). The coating was mixed (Parts A, B and C) in accordance with NASA Specification A-16839(B) and applied in successive spray coats with a 10 minute air dry between coats.

Boards A, B, and C, which received no surface treatment other than dust removal, were coated on February 14. Scattered raised spots on the coating were observed and thought to be a result of grain lifting of the plywood. Consequently, the remaining four boards (D, E, F and G) were hand sanded with 320 abrasive paper prior to coating on February 15. The sanding of these boards did not appear to make any appreciable improvement in the roughness of the applied coating. Coating thickness and number of coats applied were as indicated below in Table XXVIII. Coating thickness was determined on metal test coupons mounted alongside and sprayed with the plywood panels.

TABLE XXVIII
45B3 COATING ON PLYWOOD PANELS

Board	Coating Thickness	No. of coats applied
A	1.65 - 1.75 mm (65 - 69 mils)	7
B	1.65 - 1.75 mm (65 - 69 mils)	7
C	1.45 - 1.52 mm (57 - 60 mils)	7
D	1.42 - 1.50 mm (56 - 59 mils)	6
E	1.42 - 1.50 mm (56 - 59 mils)	6
F	1.47 - 1.52 mm (58 - 60 mils)	7
G	1.45 - 1.55 mm (58 - 61 mils)	7

V. DISCUSSION

Intumescent Salt

Procurement of intumescent salt. - A total of 362 kg (800 lbs) of the ammonium salt of 4-nitroaniline 2-sulfonic acid was purchased from Allied Chemical Corporation at \$11.00 per kg (\$5.00 per lb). This was approximately 1/4 the cost of pure ammonium salt previously available.

After some initial difficulty with sulfate content, salt, of the required purity was obtained and used to produce coatings of satisfactory quality.

Because of the particle size of the "as-received" salt, it was necessary to select a paint manufacturing technique which effected a particle size reduction.

Coating Manufacturing Methods

Manufacture of Part A of 45B3 and 313 coatings. - In reviewing the procedures employed, problems encountered and results obtained, several conclusions can be drawn regarding the three manufacturing method employed. Since the production of Parts B and C of the 45B3 and 313 coatings involved a simple blending of two liquids, the following discussion will be restricted to the manufacture of Part A (i.e., the intumescent salt, polysulfide resin and MEK mixture).

Ball milling: Ball milling afforded the best control of the three manufacturing processes used (i.e., Koruma milling, Ystral mixing with Stud-milled salt and ball milling). Salt particle size reduction, wetting of pigment, thioxotropy and elimination of air or moisture entrainment were controllable by this method.

By holding back approximately 23 percent of the required MEK and using this MEK for rinsing each mill load and by providing a small additional amount of MEK for rinsing the last load, yields of 93 percent were obtained. Since thioxotropy of Part A increases with increased milling time, the milling time was restricted to 2-1/2 hours to permit adequate rinsing. A fineness of grind between 2 and 3 was achieved by this procedure. The yield of 93 percent compared favorably with the 50 percent obtained by ball milling at Ames

Of most importance was that the ball-milled Part A produced coatings which exceeded the thermal efficiency requirements and out performed the Ystral mixed coatings (with Stud-milled salt).

Koruma Milling: Koruma milling could be employed effectively, if a relatively fine salt particle size were obtained and the premix could be kept agitated so as to supply a uniform product to the grinding stones. Some solvent losses would occur but these could be made up. A major risk is overheating of the Part A, as did happen on the first and only batch which was Koruma milled.

Ystral Mixing: Ystral mixing, using Stud-milled salt, was employed for several production lots. Although the Stud-milling of the salt (to reduce its particle size) involved an extra operation, the overall process was very efficient in terms of labor and percent yield. The yield (i.e., quantity of Part A obtained/input of raw materials) was 96 percent. Selection of this method was an expedient and was feasible only because of the relatively coarse grind permitted (i.e. 1+ fineness of grind, Hegman Grind Gage). As will be discussed later, this fineness of grind may be inappropriate. Excessive settling of the salt on storage of 45B3 Part A and very hard settling of the salt plus Refrasil in the 313 Part A may be the result of having too large a particle size and too

little thixotropy. Also, Stud-milling of the dry salt may have posed a safety hazard, since it was later learned from Allied Chemical Corp. that the dehydrated salt is subject to detonation or impact.

Addition of Refrasil into 313 coating. - As previously mentioned, the Refrasil was incorporated into Part A of 313 coating Lot 9-02-71. This material was found to have settled out very hard in several weeks of storage and was very difficult to redisperse. As a consequence, the Refrasil was packaged separately for subsequent production lots of 313 coating. This procedure had two advantages: (1) the hard settling problem was eliminated and (2) kits of 45B3 and 313 coating were now identical (formulas for the 45B3 and 313 coating are the same except for the Refrasil in the latter) allowing the available wet coating to be used as either 313 or 45B3.

The major disadvantage to the above packaging of 313 coating is the necessity of the user to add the Refrasil. Since this is not an easy procedure because of the nature of these small glass fibers, the possibility exists that the user will not exercise sufficient care, and the 313 coating will not have the desired properties. Since it would be desirable (from the user's standpoint) to incorporate the Refrasil fibers into 313 Part A during manufacture, it is suggested that the following approaches be considered to minimize the hard settling:

(1) Incorporate the Refrasil fibers into ball-milled Part A and determine whether the greater thixotropy of the ball-milled material mitigates the hard settling problem.

(2) Investigate addition of small quantities anti-settling agents (e.g. Bentones) and determine if they have a detrimental effect on thermal efficiency.

(3) Determine if a reduction in the Refrasil fiber length would minimize the settling without adversely affecting performance. Some 313 Part A material made at Ames on the Kady mill was reported to be free of hard settling. Use of the Kady mill with its high speed shearing action may have effected a significant reduction in the fiber length not experienced with the Ystral mixer.

Package Stability

Black deposits. - Analysis of the black deposits formed on the walls of the original Heresite phenolic resin coated, tinned steel pails containing Part A showed iron and tin as the major elements, presumably as the sulfide. Although the Heresite phenolic resin coating on the interior of the pail greatly reduced the quantity of black deposit formed, compared to plain tin coated steel cans, it did not completely stop the reaction.

Information received from Ames was that the black deposits were also observed in cans of Part A of 45B3 and 313 coating material manufactured in their laboratory. However, it was stated that the presence of the black deposits had no apparent effect on the thermal performance of the applied coatings.

The formation of these black deposits was eliminated by packaging Part A of the 45B3 and 313 coatings in glass containers.

Gelation. — Gelation of 45B3 Part A Lot 8-18-71 was observed in a container that had been opened several times during the six week period from the date of manufacture. The original 7.6 liter (2 gal) container was only about 40 percent full initially and about 20 percent full at the time the gelation was found. Subsequently Part A in other containers from the first lot (No. 8-18-72) of 45B3 coating were found to be gelled when inspected several weeks later.

The decision to package Part A in the 7.6 liter (2 gal) lined pails was made originally because of: (1) the problems in shipping glass containers containing highly flammable solvents (e.g. MEK), (2) the rapid reaction of Part A with unlined tinned steel, (3) the lack of available smaller containers lined with a resin coating resistant to MEK, and (4) the request to package small quantities of coating for sample distribution.

Ames reported the same gelation phenomenon with Part A of coatings produced at Ames and stored in closed containers with a large ullage. Material stored as long as 6 months in full, closed containers did not exhibit this problem and performed satisfactorily when thermally tested at Ames.

The thermal efficiency of 45B3 prepared from the previously cited can of Part A Lot 8-18-71 was only about 39 sec/mm (1.0 sec/mil) and hardly intumesced (i.e. char was only about 0.32 cm or 1/8 in.). This material was still fluid at the time the coating was prepared but was found to be gelled three days later.

At the present time the most likely explanation for the reduced thermal performance of 45B3 Lot 8-18-71 is partial polymerization of the polysulfide resin in Part A. The polymerization is probably caused by the large volume of air in the 7.6 liter (2 gal) pail and may be accelerated by metal ions from the tin coated steel. Further, lack of reactive mercaptan end groups (as was actually analyzed) when Parts A, B and C are combined, may result in less copolymerization of the epoxy and polysulfide and greater homopolymerization (i.e., cross linking) of the epoxy resin. The additional cross-linking of the epoxy would reduce thermal plasticity during heating, and make for a more rigid and smaller volume of char (as was actually observed). The net effect, of course, would be to reduce thermal efficiency.

Packaging containers. — Except for the first production lots, which were packaged in the 7.6-liter (2 gal) pails, Part A of 45B3 of 313 coatings were packaged in 0.950 liter (1 quart) glass jars. The small ullage (about 10 percent) left for expansion and mixing room was purged out with dry nitrogen before capping. The padded glass jar of Part A and the metal cans of Parts B, C and D were packed into a 3.8 liter (1 gal) friction top paint can for shipment.

If, as Ames indicated, the formation of the black deposits are not harmful, future production could utilize resin coated, tinned steel containers. However, should the black deposits be unacceptable, then a better resin coated can will have to be obtained or Part A will have to be packaged in polypropylene, high density polyethylene or glass. Whatever packaging is utilized, the containers of Part A should be full or nearly full, and users should be cautioned about storing material in containers that have substantial amounts of air space. When

a portion of Part A is removed from a full container, the material should be repackaged in a smaller container or the ullage should be swept out with dry nitrogen.

45B3 and 313 Coating Performance

Test method comparison. — Although the quartz lamp thermal efficiency heating test performed at Hughes was significantly different in operation from the fuel fired furnace test performed at Ames, the results were surprisingly similar. Both tests were performed at a heat flux of 10 Btu/ft²-sec but the fuel furnace was approximately 10 percent convective. In most cases the thermal efficiency ratings (i.e. temperature for back of the steel panel to reach 204°C (400°F)/thickness of the coating) were within 10 percent of each other. The variation from specimen to specimen was often as great as the difference produced by the two methods. Also, there was no observable trend as to which test was more severe — sometimes the quartz lamp test values were slightly higher and at other times slightly lower than the thermal efficiency rating obtained on Ames' fuel furnace.

Effect of curing procedure. — The present specifications A-16839(B) and (D) require the coating to be air dried at room temperature for 10 days minimum before testing. Except for one specimen from 45B3 Lot 11-5-71 (which was of marginal quality), coatings which were air dried for 24 hour followed by force drying at 66°C (150°F) for 16 hours appeared to be comparable to 10 day air dried coatings (see Tables XII — XXIV).

Information recently received from Ames appears to confirm that force drying at 66°C (150°F) is acceptable. Ames reported that the 24 hour air dry, before force drying, is essential to maintain good thermal performance.

Fineness of grind. — A fineness of grind (Hegman Scale) of 1+ is required by the current specifications. Fineness of grind, of course, is a measure of the largest particles in the coating and is indicative of the total particle size population. Ball milling of Part A produced a fineness of grind of 2 — 3 whereas Ystral mixing of Stud milled salt produced a 1+ grind. The fact that ball milled material with the finer grind produced coatings with better thermal efficiency ratings than the Ystral mixed coatings may be very significant.

Minimum thickness. — Thermal efficiency tests performed on 0.79 mm (31 mil) 45B3 coatings (Lot 8-18-71) indicated that the thin coatings did not afford sufficient thermal insulation during the initial stage. With these thin coatings, the back side temperature was almost at 400°F before intumescence started. Although the poor performance of this lot may be due to other factors, it would seem that the thin coating was at least a contributor.

Review of work performed under Ref.6 and discussions held with Ames Research Center support this observation relative to minimum thickness. Although one Ames prepared coating of 35 mils (see Table XVIII) had a good thermal efficiency rating at Hughes, Ames reported that coatings of 0.63 — 0.74 mm (25-29 mils) did not perform well. As a consequence, the minimum thickness for thermal efficiency testing was raised from 0.76 mm (30 mils) to 1.52 mm (60 mils).

Flexible Thermal Protection Coating

Intercoat adhesion. During preparation of the second batch of 9.45 X 9.45 cm (24 X 24 in.) flexible thermal protection sheets, a delay in the coating sequence occurred. Instead of the 10 - 15 minutes drying between successive coats, about 1-1/2 hours elapsed. After the sheets had cured, it was found that with some effort a delamination could be effected. It is strongly suspected that this reduction in intercoat adhesion was a result of the extra drying time and consequently it is recommended that the drying time between coats be limited to 20 minutes maximum.

VI. CONCLUSIONS

Intumescent Salt

(1) Ammonium salt of 4-nitroaniline-2-sulfonic acid of acceptable purity can be obtained from Allied Chemical Corp's Buffalo Dye Plant, Buffalo, N. Y.

(2) Substantial quantities (i. e. several hundred kilograms or more) can be procured thus making commercial manufacture of the Thermal Protection Coatings feasible.

(3) Reduction in cost of salt from approximately \$44.00/kg (\$20.00/lb) to present level of \$11.00/kg (\$5.00/lb) makes the commercial exploitation of the Thermal Protection Coatings practical.

Coating Manufacturing Methods

(1) Ball-milling was the best of the three methods investigated for manufacture of formulas 45B3 and 313 Part A (i. e. salt polysulfide resin, MEK mixture). Ball milling afforded the best product control and resulted in a coating which met or exceeded the required thermal efficiency of 78.8 sec/mm (2.0 sec/mil).

(2) Ball-milling is an economical method of manufacturing since mill losses were reduced to an acceptable level. Using procedures established during the program, good yields (i. e. quantity produced versus raw materials used) of 93 percent were obtained.

(3) Incorporation of Refrasil fibers into Part A of formula 313 remains a problem in terms of package stability. Packaging of the Refrasil in separate containers (to avoid the extremely hard settling experienced) should be considered an expedient and solutions to this problem should be explored.

Package Stability

(1) Formation of black deposits (probably tin and/or iron sulfides) as a result of the reaction of Part A with metal containers can be avoided by packaging in glass, polypropylene or high density polyethylene.

(2) Premature gelation of Part A was caused by excessive exposure to air due to a large ullage in the initial packaging. Metal ions and moisture may have been contributing factors. This premature polymerization can be avoided by packaging in full, or nearly full, containers or by keeping a dry nitrogen "head".

(3) Poor performance of coatings will be experienced if Part A (although still fluid) has undergone partial polymerization on storage.

Accelerated Curing of Coatings

(1) Thermal Protection Coatings 45B3 and 313 can be force dried for 16 hours at 66°C (150°F) in lieu of prolonged air drying at room temperature without impairing thermal performance. A prior air dry at room temperature (i. e. , 27°C or 80°F) for 24 hours appears to be essential.

Flexible Thermal Protection Coating

(1) Sheets of thermal protection coating with or without glass fiber mat reinforcement can be manufactured by spraying multiple coats. For best inter-coat adhesion the drying time between successive coats should be limited to 20 minutes maximum.

Materials Technology Department
Materials and Process Laboratory
Hughes Aircraft Company
Culver City, CA 90230

APPENDIX A

SULFATE AND CHLORIDE ANALYSIS PROCEDURES FOR AMMONIUM
SALT OF 4-NITROANILINE-2-SULFONIC ACID

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APPENDIX A

SULFATE AND CHLORIDE ANALYSIS PROCEDURES FOR AMMONIUM SALT OF 4-NITROANILINE-2-SULFONIC ACID

Sulfate Determination

1. Weigh out approx. 10g of salt sample in 2 liter beaker.
2. Dissolve in 1 liter of distilled water.
3. Stir until dissolved (warm the solution as required).
4. Filter through Whatman #40 filter paper.
5. Rinse the filter paper with 50 ml of distilled water.
6. Add 25 ml of conc. HCl.
7. Heat to boiling.
8. Add 75 ml of 10% $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution.
9. Keep at 90°C for 10 min.
10. Filter through Whatman #40.
11. Rinse with hot distilled water until free of chloride when tested with AgNO_3 solution.
12. Place the filter paper in a tared crucible.
13. Expose the crucible to $600 - 800^\circ\text{C}$ until constant weight of BaSO_4 is obtained.

Chloride Determination

1. Weigh out approx. 10g of salt sample in 2 liter beaker.
2. Dissolve in 1 liter of distilled water.
3. Stir until all the salt dissolves. Warm as required for complete solution of the salt.
4. Filter through Whatman No. 40 filter paper.
5. To filtered solution, add 5 ml of Conc. HNO_3 .
6. Heat just to boil and add 25 ml of 1N AgNO_3 solution.

7. Heat to boil while stirring vigorously (approx. 5 min.)
8. Allow to stand at ambient temperature overnight.
9. Filter through sintered porcelain filtering crucible.
10. Wash thoroughly with dil. HNO_3 and then with distilled water.
11. Expose the crucible to approx. 300°C until constant weight of AgCl is obtained.

APPENDIX B
RESIN, CURING AGENT AND SOLVENT QUALIFICATION
PER SPECIFICATION A-16839 (A)

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APPENDIX B

RESIN, CURING AGENT AND SOLVENT QUALIFICATION PER SPECIFICATION A-16839 (A)

HUGHES-NASA (PO-04-334327-FD3) THIOKOL LP-3 THIOKOL CHEMICAL CORP. Lot #239M

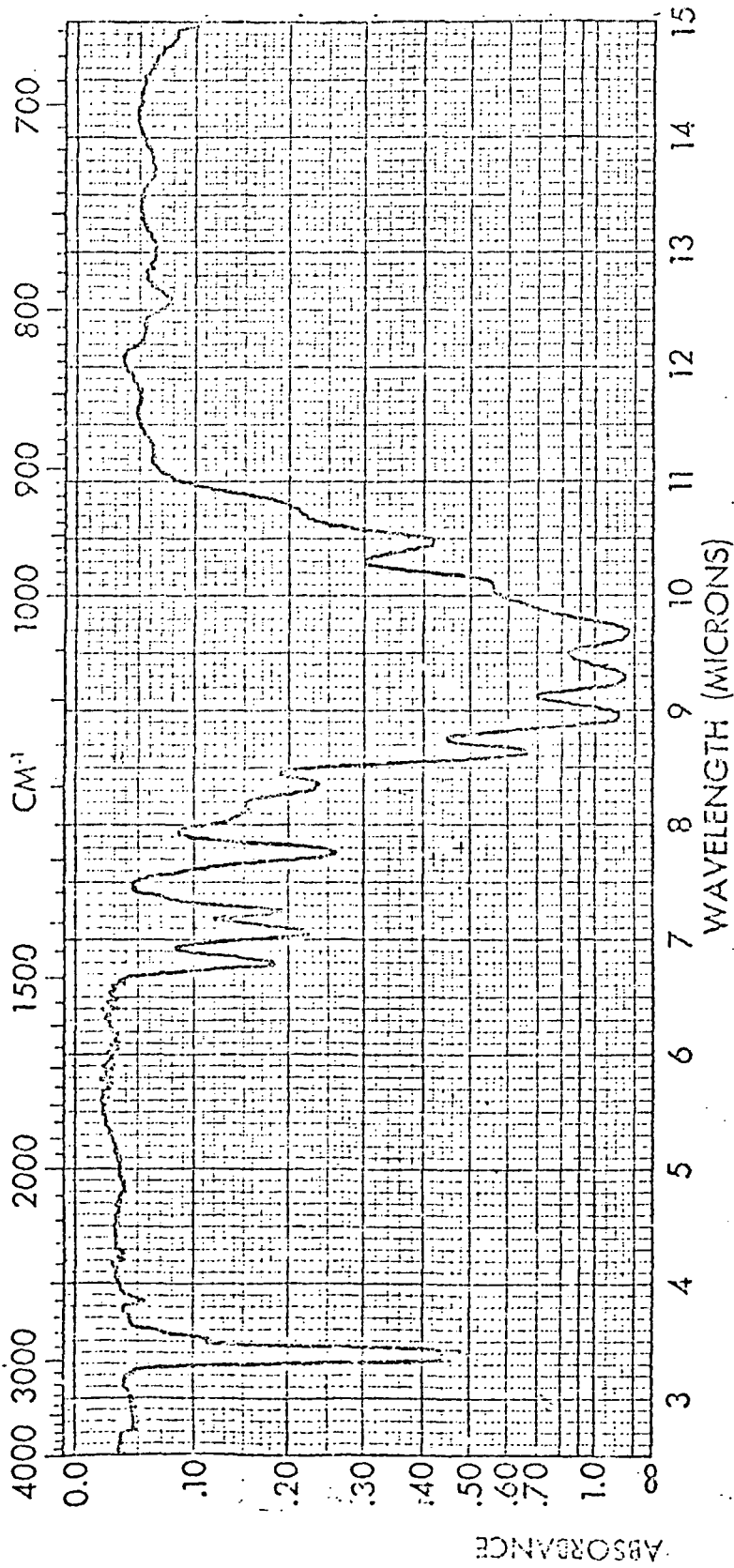
	<u>Test Method Reference</u>	<u>Limits</u>	<u>Results</u>
IR Scan	Para. 3.1.3.2		C.K. per Figure 1
Appearance:	Para. 3.1.3.3.1.1		Clear Amber, No phase separation No suspended particles
Specific Gravity g/cc	Code LF-241*	1.260-1.283	1.273
Color (Hellige)	Code LF-241*	12 Maximum	11
Viscosity (80° F cps)	Code LF-241*	700-1200	965
PH (H ₂ O extract)	Code LF-241*	6.0-8.0	6.9
Moisture Content, %	Code LF-241*	0.1 Maximum	0.06
Mercaptan, %	Code LF-241*	5.9-7.7	6.86

*Thiokol Chemical Corp. Product Specification 6/2/71
Charles G. Pease
JP2-56-57

	<u>Test Method Reference</u>	<u>Limits</u>	<u>Results</u>
IR Scan	Para. 3.1.3.2		O. K. per Figure 1 **
Appearance	Para. 3.1.3.3.1.1		Clear Amber, No phase separation No suspended particles
Specific Gravity g/cc	Code LF-241 *	1.260-1.283	1.272
Color (Hellige)	Code LF-241 *	12 Maximum	12
Viscosity (80° F cps)	Code LF-241 *	700-1200	1000
PH (H ₂ O extract)	Code LF-241 *	6.0-8.0	7.3
Moisture Content, %	Code LF-241 *	0.1 Maximum	0.05
Mercaptan, %	Code LF-241 *	5.9-7.7	6.93

* Thiokol Chemical Corp. Product Specification

** IR Scan performed by Hughes
2/25/72
Charles G. Pease
JP3-97



SPECTRUM NO. _____	ORIGIN <u>Eurate Plastic</u>	LEGEND _____	REMARKS <u>See 1-11</u>
SAMPLE <u>JE 2 A</u>		1. _____	
<u>1-2-3 POLYSULFIDE</u>	PURITY _____	2. _____	
RESIN LOT # <u>289M</u>	PHASE <u>liquid</u>	DATE <u>5/30/71</u>	
	THICKNESS <u>511</u>	OPERATOR <u>H. LEWIS</u>	

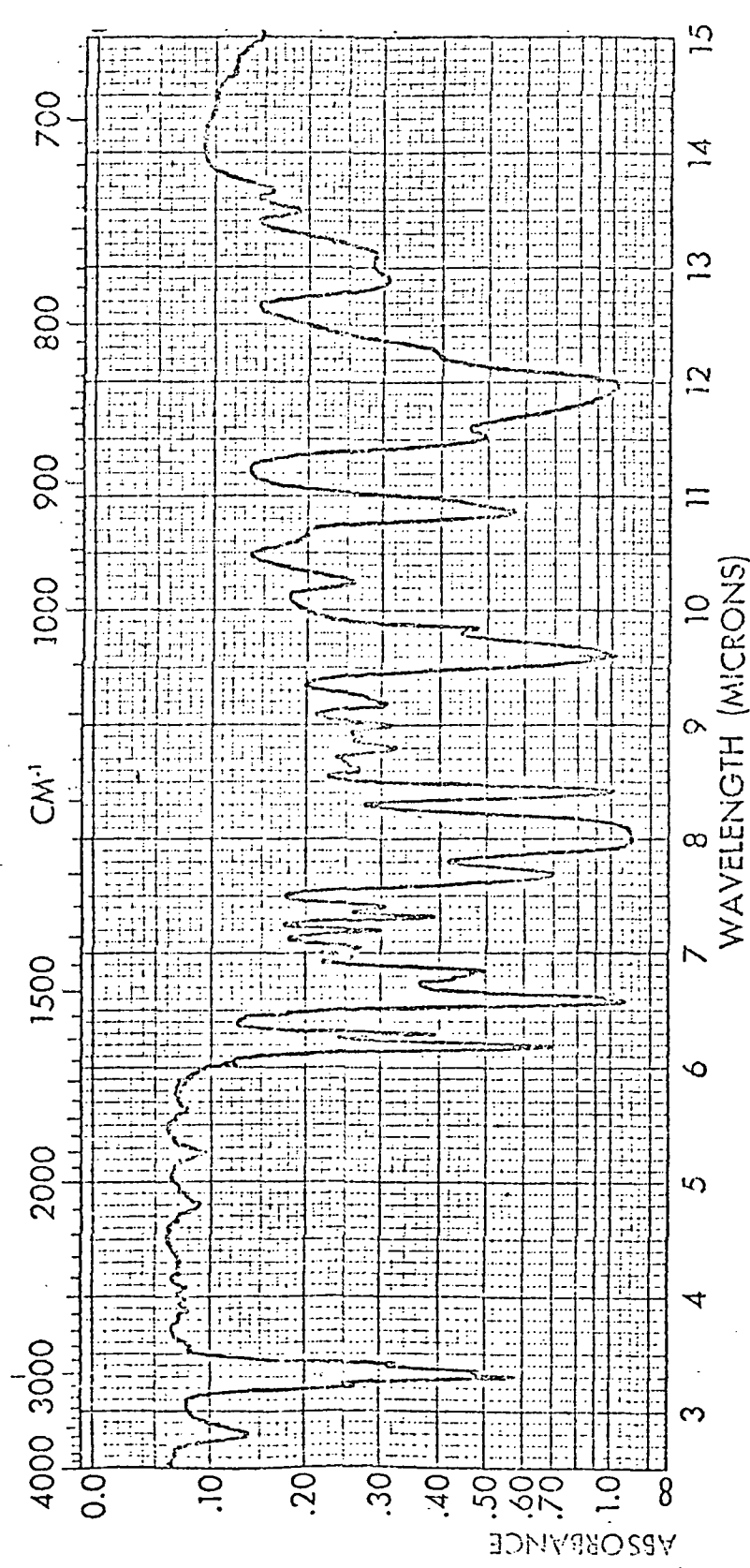
APPENDIX B

RESIN, CURING AGENT AND SOLVENT QUALIFICATION PER SPECIFICATION A-16839 (A)

HUGHES-NASA (PO-04-334327-FD3) EPON 828 SHELL CHEMICAL CO. Lot #2PHJ27

	<u>Test Method Reference</u>	<u>Limits</u>	<u>Results</u>
IR Scan	Para. 3.5.3.2		O. K. per Figure 3
Appearance	Para. 3.5.3.31.1		Light yellow, No phase separation No suspended particles
Color (Gardner)	ASTM D-1544	4 Maximum	3
Viscosity (Poise)	ASTM D-445	100-160	137 (Run on Brookfield #5 Spindle 10 RPM) 133 Kinematic, #600 Viscometer at 80°F (Cannon Fenske Tube)
Density g/cc	ASTM D-1217	1.168 ± 0.005	1.166
Refractive Index	ASTM D-1747	1.570 - 1.575	1.572
Flash Point °F	ASTM D-1310	175 min.	400+
Epoxide Equivalent	ASTM D-1652	185-192	188
Average Mol. Wt.	SC 60-146R*	380 approx.	376
Chemical Structure	SC 60-146R*		Epichlorohydrin/Bisphenol A Type Epoxy Resin

* Shell Chemical Co. Data Sheet



SPECTRUM NO. _____	ORIGIN <u>Ethane Plastic</u>	LEGEND _____	REMARKS _____
SAMPLE <u>JP 2 B</u>		1. _____	
<u>E 628</u>		2. _____	
<u>LOT # 2PHJ27</u>	PURITY _____	DATE <u>5/30/71</u>	
	PHASE <u>liquid</u>	OPERATOR <u>L. Johnson</u>	
	THICKNESS <u>411n</u>		

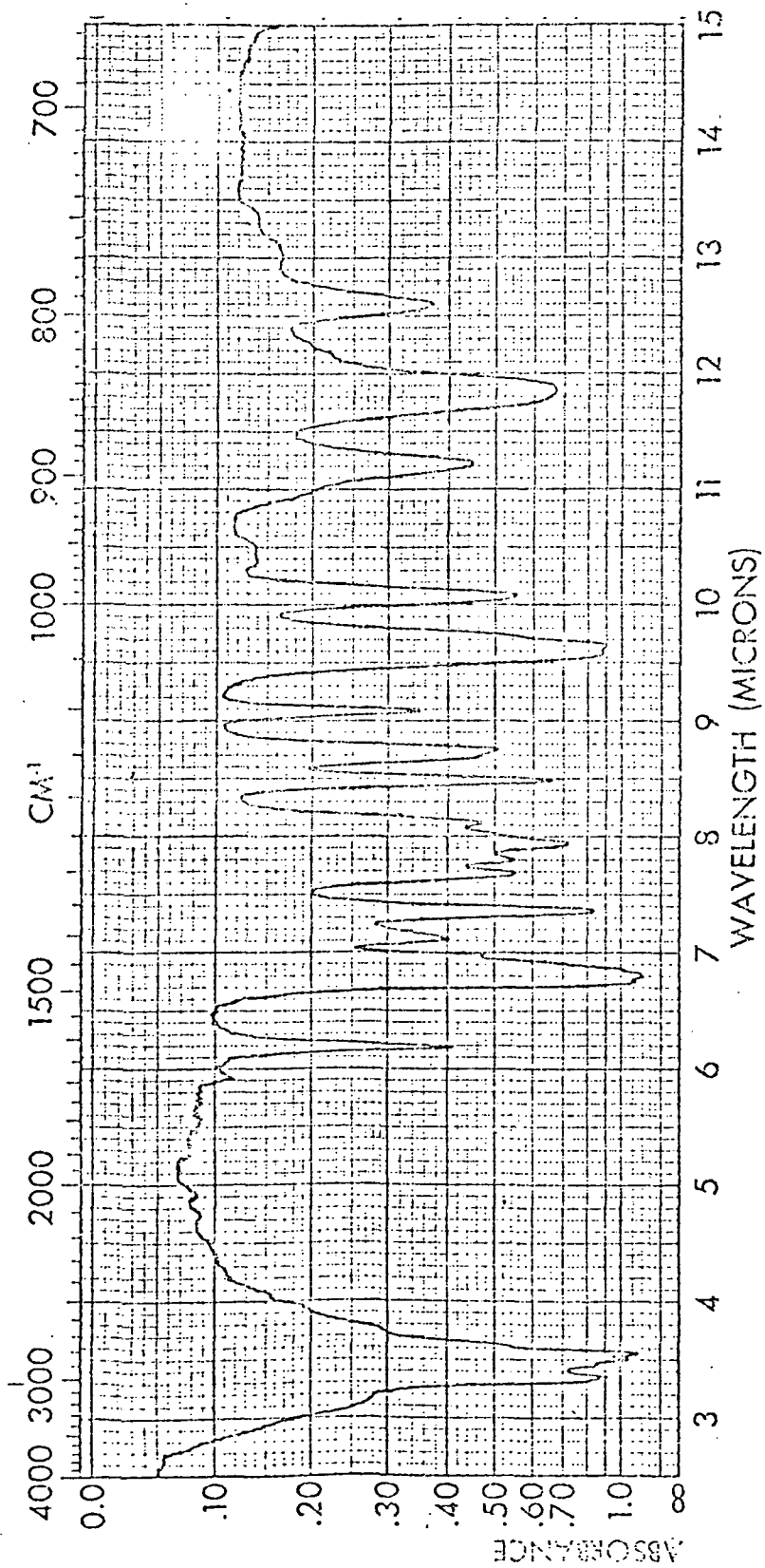
APPENDIX B

RESIN, CURING AGENT AND SOLVENT QUALIFICATION PER SPECIFICATION A-16839 (A)

HUGHES-NASA (PO-04-334327-FD3) DMP-30 ROHM HAAS CHEMICAL CO. Lot #2-9774

	<u>Test Method Reference</u>	<u>Limits</u>	<u>Results</u>
IR Scan	Para. 3.6.3.2		O.K. per Figure 4 Spec. A-16839 (A)
Appearance	Para. 3.6.3.3.1.1		No Phase Separation No Suspended Particles
Density, g/cc	ASTM D-941	0.973 ± 0.002	0.974
Flash Point, °F	ASTM D-56	315 (Min.)	348
H ₂ O Content, %	ASTM E-203	0.06 Max.	0.012

6/2/71
Charles G. Pease
JP2-63



SPECTRUM NO. _____	ORIGIN <u>Furane Plastics</u>	LEGEND _____	REMARKS _____
SAMPLE <u>JP 2 C</u>		1. _____	
<u>Dir. 30</u>	PURITY _____	2. _____	
<u>Lot # 2-9774</u>	PHASE <u>liquid</u>	DATE <u>May 30, 71</u>	
	THICKNESS <u>film</u>	OPERATOR <u>L. Johnson</u>	

APPENDIX B

RESIN, CURING AGENT AND SOLVENT QUALIFICATION PER SPECIFICATION A-16839 (A)

HUGHES-NASA (PO-04-334327-FD3) MEK MC KESSEN CHEMICAL CO. Lot #----

	<u>Test Method Reference</u>	<u>Limits</u>	<u>Results</u>
Appearance	Para. 3.3.3.2.1		Clear - No Sediment No suspended matter
Alcohol Content by Weight, %	ASTM D-1362	0.7 Maximum	0.48
Specific Gravity, g/cc	ASTM D-268	0.805-0.807	0.806
Non-Volatile Matter 100 ml., gram	ASTM D-1353	0.0005 Maximum	0.0003
Acidity, Mg KOH/gm of sample	ASTM D-1613	0.047 Maximum	0.035
Distillation, Below 78.5°C Above 81.0°C	ASTM D-1078	None None	None None
Color, Cobalt-Platinum Scale	ASTM D-1209	10 Maximum*	Less than 10
H ₂ O Content, % by Weight	ASTM D-1364	0.3 Maximum	0.12

6/2/71
Charles G. Pease
JP2-58-60

*TT-M-261"D" limits color to 10 max, TT-M-261"C" limits color to 20 max.

APPENDIX B

RESIN, CURING AGENT AND SOLVENT QUALIFICATION PER SPECIFICATION A-16839 (A)

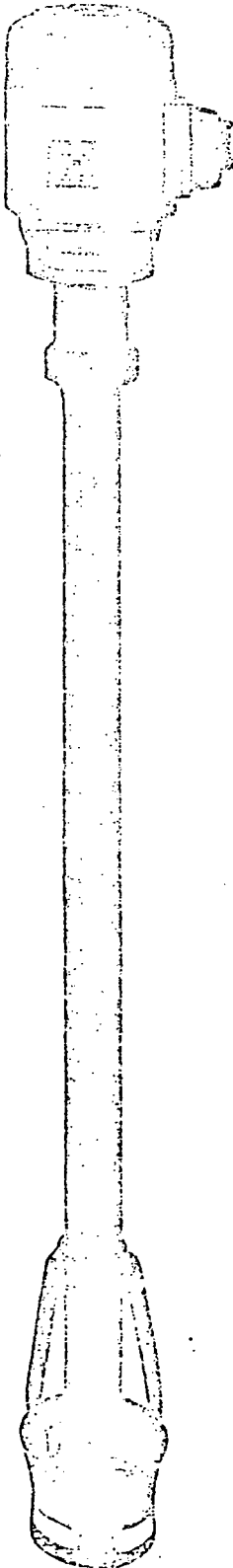
HUGHES-NASA (PO-04-334327-FD3) TOLUENE L. T. SAWYER CO. Lot # _____

	<u>Test Method Reference</u>	<u>Limits</u>	<u>Results</u>
Appearance	Para. 3.4.3.2.1		Clear, No sediment No suspended matter
Acidity	ASTM D-847	None	None
Color, Platinum-Cobalt Scale	ASTM D-1209	20 Maximum	Less than 20
Color, 0.003 g/l Potassium Dichromate	Table 5	Equal or lighter	Lighter
Sulfur Compounds, SO ₂ H ₂ S	ASTM D-853	None None	None None
Specific Gravity	ASTM D-891	0.860 - 0.870	0.861
Boiling Point, °C	ASTM D-850	109 Min.	109.5
Dry Point, °C	ASTM D-850	113 Max.	111.0
Total Distillate, % by Volume	ASTM D-850	97 Min	97.5
Aromatic Hydrocarbons, % by Volume	ASTM D-850	96 Min.	97.0
Chemical Formula	Para. 3.4.3.2.2		C ₆ H ₅ CH ₃
Mol. Weight	Para 3.4.3.2.2	92.13	92.13

6/2/71
Charles G. Pease

APPENDIX C
SPECIAL MANUFACTURING EQUIPMENT

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dissolving homogenizing emulsifying dispersing suspending

Practical experience confirms that results arrived at with YSTRAL represent highest grade qualities which are an irrevocable prerequisite for their final realization.

This prospect can give information only about construction and operation methods of the jet mixer turbine YSTRAL. Versatility, variety of service and scope make it impossible to show the various problems and their solution by means of YSTRAL in detail. For this purpose special information leaflets as well as our consulting service are placed at your disposal. The latter will be glad to render any information as to particulars.

YSTRAL is characterized by

■ a jet mixing head with suction funnel working in accordance with the injector principle, producing ■ a continuous and controlled vertical flow towards the container bottom and

■ preventing even the smallest air particles being locked in.

■ By means of the controlled flow each single particle of the components in process will be conducted into the jet chamber. During their passage the essential homogenizing or emulsifying process is taking place in the "pressure chamber" produced by the rotor and stator.

■ Mode of operation: The constructional feature of the jet mixer turbine YSTRAL – based on the injector principle – is a stationary control ring which surrounds the rotating propeller. This control ring can be adjusted according to the degree of viscosity of the substances to be mixed. It counteracts centrifugal forces produced by the propeller which would separate substances differing in specific weight. By these means the specifically heavier components are prevented from being flung on to the container walls where they would stick and eventually settle on the bottom. By this procedure a homogeneous mixture throughout, even of specifically very different heavy components, is obtained.

The control ring is funnel-shaped on top in order to obtain the required intensive suction and the exact vertical guidance of the flow. The contents of the container are sucked up, controlled for homogeneity from all directions and then directed into the jet chamber. The powerful sealed jet ejected from the jet chamber reaches down to the container bottom where it is deflected to the wall, thrown back to the surface, to be picked up again by the suction of the jet mixing head. Within a few seconds a continuous circulation begins which stirs the total contents of the container without leaving any dead spots. Also very viscous substances or heavy particles deposited on the container bottom as a consequence of long storage are washed away by the jet, circulated, carried to the top and homogeneously blended with the other components of the mixture in the container.

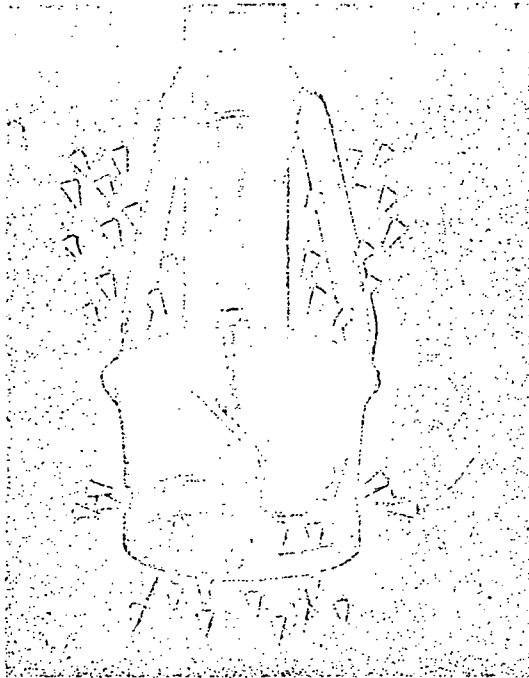
■ Position of the jet-mixer YSTRAL: In case of low-viscosity media being applied the propeller has to be placed in position in the upper, closed part of the control ring. In this position the mixing head functions as a double injector. Hereby additional suction is taking place by means of the perforated extension in the lower range of the control-ring. Thus also the axial thrust is also being reinforced.

In case of high-viscosity substances being applied the rotor has to be brought into position in the lower part of the stator. Congestion – which in case of high-viscosity media necessarily develops within the ring-chamber – will be prevented for the reason that part of the substance can drain off on the side through the slots; thereby an uninterrupted continuous flow-through is insured.

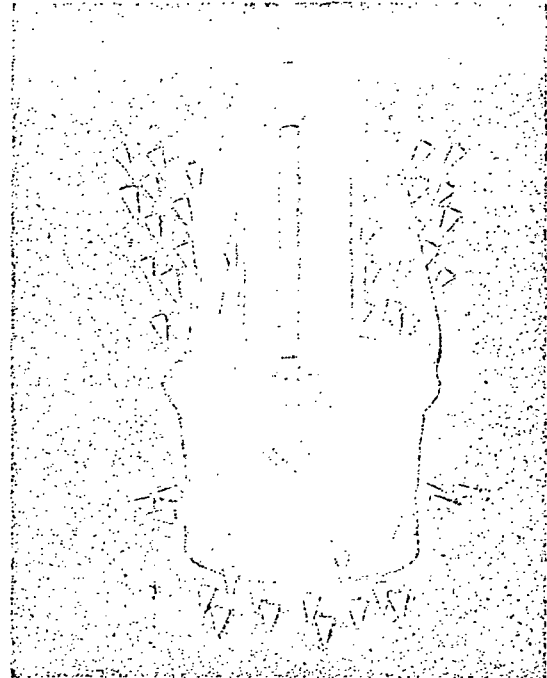
■ Rotating cone: The truncated cone type rotating between bearing pipe and propeller outside the control ring serves the purpose to accelerate the flow of the substance which is being sucked into the stator. It also intensifies the power of the jet which is ejected towards the bottom.

Figure C-1. Ystral Jet Mixer

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Adjustment
of Jet Mixing Head for low viscosity substances



Adjustment
of Jet Mixing Head for high viscosity substances.

■ **No air absorption** Complete absence of air in YSTRAL is guaranteed by the sealed guide tube which reaches down to the mixing head. Thus the rotating shaft has no contact with the substances to be mixed and no air can penetrate into the mixture.

■ **Ventilation** The steady and continuous vertical flow produces the ventilation of substances which have absorbed air in the course of a preceding part of the operation.

■ **Position of the jet mixing turbine YSTRAL** Best mixing results are obtained when YSTRAL is placed in the container alongside the container wall. If this proves impossible, it should at least be placed eccentrically in the container. At any rate, never should the mixing head be placed too near to the container bottom. If the mixing head operates too near to the bottom the impulse of the ejected jet will be retarded. Thus its thrust will be impaired and the effect will be impaired.

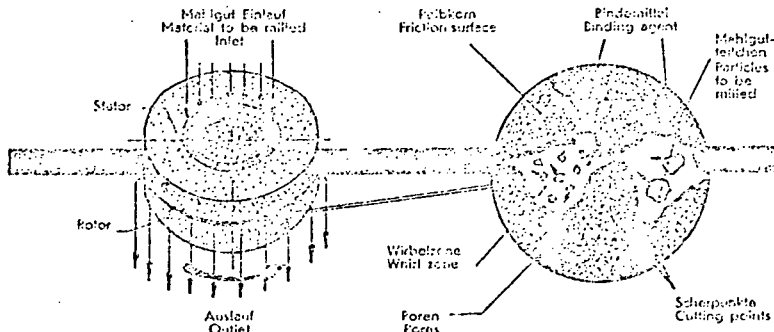
■ **Containers** Owing to the intensive and controlled circulation, the shape of the container to be used is of no importance. Its diameter may be considerably greater than its height. It is also unimportant whether its form is circular or rectangular and whether it has a conical bottom or not. Furthermore, it is not necessary that container and mountings are exceedingly sturdy in as much as the axial thrust caused by the jet considerably relieves the stress of weight of YSTRAL and of the mounting attachments.

■ **Emulsions** In the course of these instructions special mention should be made of the often difficult field of preparation and production of emulsions.

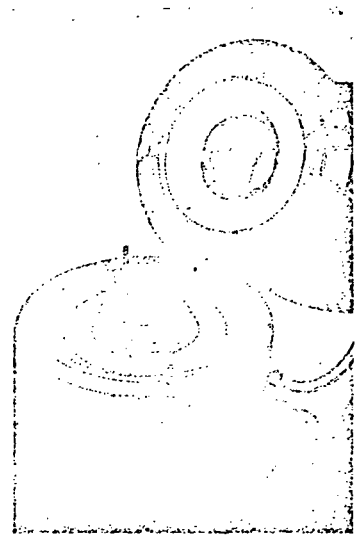
The "pressure chamber" formed within the jet chamber is in a position to produce easily emulsions (W/O-type) from pure oil and pure water without air impact which are of adequate permanence. The water will be completely "beaten" into the inner phase without leaving even a particle of water unemulsified between the phases. Operating without air in the production of emulsions is of special importance in as much as air distributed in countless numbers of little bubbles in the medium makes the emulsion spongy and unstable.

Figure C-1. Ystral Jet Mixer (Concluded)

Korundmahlsteine Bei vielfacher Vergrößerung der Korundsteinoberfläche gleicht diese einer Landschaft von Gebirgen. Bei der Arbeit der Steine gegeneinander sind die Gipfel die dort, wo die Spitzen der Berge sich treffen, an denen das Mahlgut zerdrückt wird. Die gegenüberliegenden Täler bilden Hohlräume, wir nennen sie Wirbelzonen, in die das Material zur Feinbelichtung kommt.



Corundum mill stones When greatly magnified, the surfaces of the corundum mill stones look like a mountainous landscape. As the stones work against each other, the peaks of the mountains meet and create the cutting points, where the material is crushed. In the same way, as the valleys face each other, they form hollows, called whirl zones, where the material is further processed.



Fineness of milling and heating are two main problems when processing many products.

The Koruma mills solve both these problems because of the very wide range with regard to fineness of milling and the degree of heating. This latitude is the reason for the great versatility of the machine which is still being extended.

Fineness of the end product.
Koruma mills can be used for breaking up or rough milling, but also for grain sizes down to 1 micron. The required degree of fineness is obtained by means of the milling stone gap and by selection and combination of milling stone granulation (7 different granulations are available).

Heating
In order to prevent excessive heating of the product, all mills, from type 1 onwards, are equipped with a cooling installation. The types 3 K and 4 K (see 3 K and 4 K) are designed for particularly sensitive materials to be milled.

Method of operation: -

The heart of our mills is formed by the two corundum mill stones, which are placed horizontally, one above the other, and are supplied with different granulations and hardness. The lower revolving mill stone (rotor) rotates 3000 r.p.m. against the upper, fixed mill stone (stator). The material to be milled flows between the two stones, and it is taken by means of suitable feed attachments and the centrifugal force of the mill stones from the hopper or feed pipe through the opening in the middle of the stator to the centre and from there to the periphery of the stones. During its passage, the material is crushed and broken up at the cutting points of the granular mill stones. The forces of cavitation in the eddy zones further reduce, mix or homogenise, disperse and emulsify the material. Substances to be milled which have a liquid plus a solid phase, are very well moistened or dispersed.

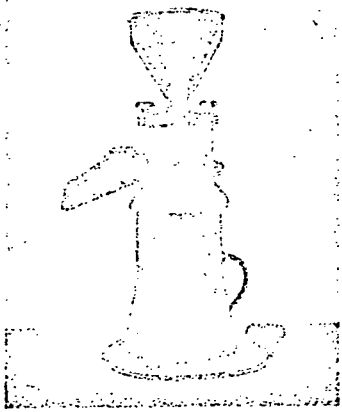
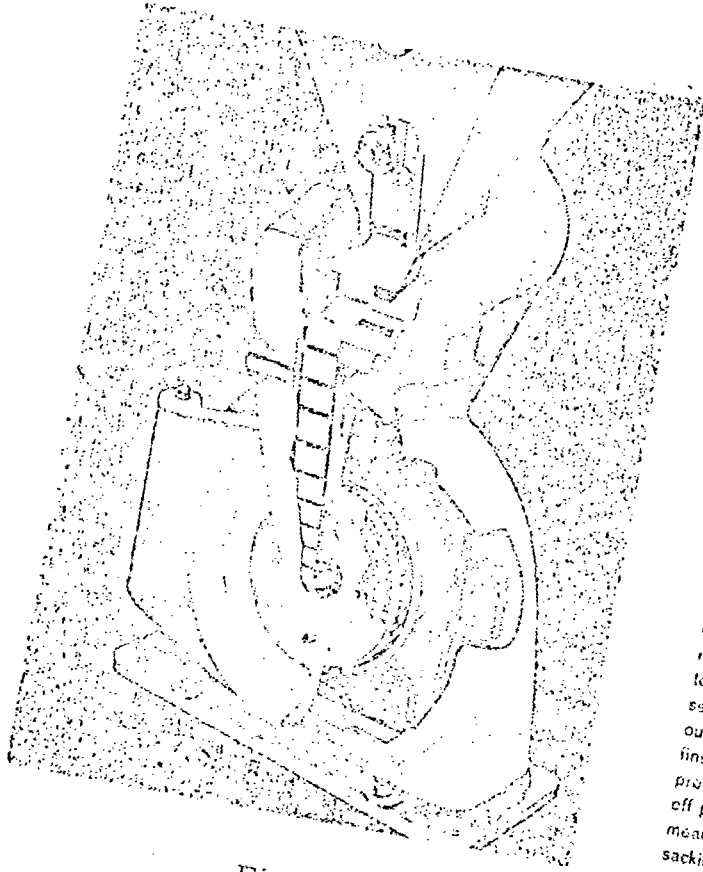


Figure C-2. Koruma Mill



Method of operation

The material, fed-in continuously, is carried over a high efficiency magnetic separator. Due to the air stream in the intake funnel of the mill door the product to be ground is taking its way through the fixed stud disc and sucked centrally into the grinding chamber where it is seized by the rotating disc and distributed uniformly to all sides. While passing progressively on its tortuous path through the different rows of intermeshing studs, the material is exposed, in free flow, to the impact action until being carried into the spacious grinding chamber as soon as it has been sufficiently reduced. The housing whose shape is adapted to the flow lines of the material to be processed, allows the fines-laden air stream to be let out freely through a large bottom opening. The fines are received in a sacking-off container provided immediately beneath or are sucked-off pneumatically or conveyed by mechanical means. The grinding air escapes from the sacking-off container through a filtering plant or a cyclone arranged separately.

Figure C-3. Kolloplex Stud Mill,
Model 160z (Alpine American Co.)

REFERENCES

1. Specification No. A-16839 (E) Rev. 1. "Preliminary Material Specification for Ammonium Salt of 4-Nitroaniline-2-Sulfonic Acid", Chemical Research Projects Office, NASA-Ames Research Center, (Moffett Field, California 94035)
2. Specification No. A-16839 (A) "Preliminary Material Specification for 45B3 Thermal Protection Coating", Chemical Research Projects Office, NASA-Ames Research Center, (Moffett Field, California 94035)
3. Specification No. A-16839 (C) "Preliminary Material Specification for 313 Thermal Protection Coating", Chemical Research Projects Office, NASA-Ames Research Center, (Moffett Field, California 94035)
4. Specification No. A-16839 (D) "Preliminary Process and Application Specification for 313 Thermal Protection Coating", Chemical Research Projects Office, NASA-Ames Research Center, (Moffett Field, California 94035)
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