MILITARY SPECIFICATION

HYDROXYL-TERMINATED POLYBUTADIENE

This specification is approved for use by the Naval Air Systems Command, Department of the Navy, and is available for use by all Departments and Agencies of the Department of Defense.

1. SCOPE.

1.1 Scope. This specification establishes the requirements for two types of hydroxyl-terminated polybutadiene (HTPB).

1.2 Classification. The HTPB shall be of the following types:

Type I	Without Antioxidant.
Type II	With Antioxidant.
Class 1	With Antioxidant, 2,2'-Methylenebis (4-Methyl-6-T-Butylphenol).
Class 2	With Antioxidants, N-Phenyl-N'-Cyclohexyl-P-Phenylene Diamine and 2,5-Di-T-Butyl Hydroquinone.

2. APPLICABLE DOCUMENTS.

2.1 Issues of documents. The following documents of the issue in effect on date of invitation for bids or request for proposal form a part of this specification to the extent specified herein.

Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Commanding Officer, Naval Air Engineering Center, Engineering Specifications and Standards Department (ESSD), Code 93, Lakehurst, NJ 08733, by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

FSC 6810

SPECIFICATIONS

MILITARY

MIL-A-85495	Antioxidant, 2, 2'-Methylenebis (4-Methyl-6-t-Butylphenol).
MIL-A-85501	Antioxidant, N-Phenyl-N'-Cyclohexyl-P-Phenylene Diamine.

STANDARDS

MILITARY

MIL-STD-129	Marking for Shipment and Storage.
MIL-STD-1218	ACS Chemicals.

DRAWINGS

Naval Air Systems Command
(Code Ident 30003)

639AS4608	Antioxidant, Hydroquinone Type.

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specified procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

3. REQUIREMENTS.

3.1 Formulation. The formulation of Type II HTPB shall consist of a blend of Type I HTPB and antioxidants. Type II, Class 1 polymer contains the antioxidant specified in MIL-A-85495. Type II, Class 2 polymer contains a 50:50 mixture (by weight) of the antioxidants specified in MIL-A-85501 and Drawing 639AS4608, respectively.

3.2 Chemical and physical properties. Chemical and physical properties of the polymers shall conform to Table I.

TABLE I. Chemical and physical properties.

Property	Type I		Type II	
	Min	Max	Min	Max
Hydroxyl, eq/100 grams	0.070	0.080	0.075	0.085
Moisture, percent	...	0.10	...	0.10
Peroxide, as H_2O_2, percent	...	0.10	...	...
Viscosity, poise at 25°C	40	70	40	80
Molecular weight (GPC)	2,500	3,600	...	...
Antioxidant, percent by weight	...	...	0.9	1.1

3.3 Stability. When packaged in accordance with 5.1 and stored at temperatures less than 38 degrees Celsius (°C), the Type I and Type II HTPB shall meet the requirements of this specification for a minimum of 12 months after acceptance. The shelf life may be extended for 6-month intervals after reacceptance testing for conformance to requirements of hydroxyl, moisture, and viscosity (Type I and Type II) and antioxidant (Type II only) of Table I.

3.4 Type II HTPB. Type II, Class 1 and Class 2 HTPB shall be made from Type I HTPB which conforms to all the requirements of this specification and shall meet the hydroxyl, moisture, viscosity, and antioxidant limits of Table I after blending.

3.5 Toxic products and safety. Safety regulations and guidelines applicable to the use of HTPB should be complied with to preclude personal injury and damage to equipment and facilities.

3.6 Workmanship. Workmanship shall be such that HTPB is uniform, of consistent high quality and free from visible contamination.

4. QUALITY ASSURANCE PROVISIONS.

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order (see 6.2.1), the contractor shall be responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the contractor may utilize his own facilities or any commercial laboratory acceptable to the Government. The Government reserves the right to perform any of the inspections set forth in this specification where such inspections are deemed necessary to assure that supplies and services conform to prescribed requirements.

4.2 Sampling. The lot shall be sampled in accordance with Table II.

TABLE II. Sampling plan.

Number of containers in lot	Number of containers sampled (primary sample)	Number of composite samples
100 or more	10% (nearest whole number)	5
51 - 99	10	4
11 - 50	10	3
1 - 10	All	2

4.2.1 Primary samples. Physical properties tests shall be run on each primary sample (see Table II). The material container may be sampled by use of a clean glass tube, rod, or pipet. If the container is small enough to be handled safely, the sample may be obtained by pouring. The smallest sample size possible that is consistent with test requirements shall be taken. The minimum sample size shall be two ounces. Glass containers shall be used for all liquid samples. Each sample shall be labeled with date, lot number, and manufacturer's container identification number. Failure of any primary sample to pass all of the physical-properties tests herein shall result in rejection of the lot represented.

4.2.2 Composite samples. Chemical properties tests shall be run on each composite sample. Divide the primary samples equally into the number of composites shown in Table II. Blend each composite throughly by manipulation of the container. Label each composite with Roman numerals, also include date, lot numbers, and manufacturer's container identification numbers. The remainder of the primary samples shall be retained pending acceptance or rejection of the lot. Failure of any composite sample to pass all of the chemical-properties tests herein shall result in rejection of the lot represented.

4.3 Quality conformance inspections and tests. Quality conformance inspections and tests shall consist of the following:

a. Tests of Table I properties (see 4.4).

b. Inspection of filled containers (see 4.6.1).

c. Visual inspection (see 4.6.2).

4.4 Tests methods. Tests shall be performed using apparatus, reagents, and procedures specified herein. The use of alternate apparatus, reagents, or procedures shall require prior written approval of the procuring activity. All American Chemical Society (ACS) reagents shall conform to MIL-STD-1218.

4.4.1 Hydroxyl equivalents/100 grams.

4.4.1.1 Apparatus.

a. Iodine flask, 125-milliliter (ml).

b. Micro buret, 10-ml.

c. Steam bath.

4.4.1.2 Reagents.

a. Acetic anhydride, ACS.

b. Pyridine, ACS.

c. Standardized alcoholic sodium hydroxide, 0.2 normal (N), prepared by diluting 15 ml of 50 percent NaOH (aqueous) with ethanol to 1 liter. Standardize against potassium acid phthalate

d. Phenolphthalein, 1 percent in ethanol.

4.4.1.3 Determination of hydroxyl equivalents/100 grams (gm). Weigh accurately 1.0 gm of sample into a 125-ml iodine flask. Weigh 1.0 gm of sample into another similar flask for acid value. Pipet accurately 5 ml of acetic anhydride-pyridine mixture.

NOTE: Acetic anhydride-pyridine mixture deteriorates on standing.

Prepare fresh mixture, 1 part acetic anhydride to 31 parts pyridine, of sufficient quantity for daily needs) into each of two flasks, the sample flask and another similar flask for the blank. Swirl to dissolve the sample (flask may be warmed if necessary), moisten the stopper with pyridine and insert loosely into the flask. Pipet 8 ml of pyridine into the acid value flask. Place all flasks onto a steam bath and heat for 2 hours. At the end of this period, add 2 ml of distilled water to each flask and continue heating for 10 minutes. Remove flasks from the bath and allow to cool to room temperature. Add 50 ml of pyridine to each flask, making sure that the walls of the flasks are washed down. Swirl

to dissolve the sample (flask may be warmed if necessary). Add 1 ml of phenolphthalein indicator to each flask and titrate to a persistent pink with standardized alcoholic sodium hydroxide solution.

Calculation:

$$\text{Hydroxyl equivalents/100 gm} = \frac{(A + \frac{B \times C}{D} - E)\ N}{10 \times B}$$

where

A = volume of sodium hydroxide for blank, ml

B = weight of sample, gm

C = volume of sodium hydroxide for acid value, ml

D = weight of sample for acid value, gm

E = volume of sodium hydroxide for sample, ml

N = normality of sodium hydroxide

Report the hydroxyl equivalents/100 gm to the nearest 0.0001 unit.

4.4.2 Moisture.

4.4.2.1 Apparatus. Beckman "Aquameter," Model KF-4, or equal.

4.4.2.2 Reagents.

a. Pyridine, ACS reagent.

b. Chloroform, ACS reagent.

c. Karl Fischer (KF) reagent, stabilized, water equivalent of 2.0 to 3.0 milligrams/milliliter (mg/ml).

4.4.2.3 Determination of moisture. To the reaction beaker containing 60 ml of 1:1 neutralized pyridine-chloroform solution, add from a disposable syringe 5 to 8 gm of sample which is weighed by difference to the nearest 0.01 gm. The stirrer should be off while adding the sample.

Turn on the stirrer to the same position used in the neutralization. Titrate automatically by pressing the titrate button to a 30-second end point.

Calculation:

$$\text{Percent moisture} = \frac{V \times E}{10 \times W}$$

where

V = volume of KF reagent, ml

E = water equivalent of KF reagent, mg/ml

W = weight of sample, gm

Report the moisture to the nearest 0.01 percent.

4.4.3 Peroxide.

4.4.3.1 Apparatus.

a. Buret, 25-ml.

b. Reflux condenser, 300-millimeter (mm), with 24/40 tapered stopper joints.

c. Heating mantle, 250 ml, Glas Col, or equal.

d. Flat bottom flask, 250-ml with 24/40 tapered stopper joint, or equivalent.

e. Magnetic stirrer, variable speed, with Teflon coated stirring bars, or equal.

f. Ice or cold water bath.

4.4.3.2 Reagents.

a. Glacial acetic acid, ACS reagent.

b. Chloroform, ACS reagent.

c. Potassium iodide solution (20 gm KI/100 ml of water-methanol 1:3).

d. Standardized sodium thiosulfate solution, 0.01 N.

e. Indicator, (Thyodene, Magnus Chemical Company), or equal.

4.4.3.3 Determination of peroxide. Weigh accurately 5.0 gm of sample into a 250-ml flask. Add 25 ml of chloroform, 5 ml of glacial acetic acid, and 10 ml of potassium iodide solution. Add a stirring bar and attach the flask to the reflux condenser. Boil the contents of the flask for 3 minutes while stirring. Cool immediately in an ice bath or cold water bath. Wash down the condenser and sides of the flask with 25 ml of distilled water. Add 0.4 gm of thyodene and titrate with standardized sodium thiosulfate solution until one drop makes the solution clear.

Calculation:

$$\text{Peroxide, as } H_2O_2, \text{ percent} = \frac{V \times N \times 3.4}{W}$$

where

V = volume of sodium thiosulfate, ml

N = normality of sodium thiosulfate

W = weight of sample, gm

Report the peroxide to the nearest 0.01 percent.

4.4.4 Viscosity.

4.4.4.1 Apparatus.

a. Viscometer, Brookfield, Model HBF, multispeed, with spindle number 2, or equal.

b. Water bath with thermostatic control to ±0.1°C in the range from 20 to 50°C.

4.4.4.2 Reagent. Standard viscosity oil, OB type, National Bureau of Standards or equal for viscometer calibration at 25°C.

4.4.4.3 Standardization of viscometer. Using the standard viscosity oil as sample, and following the procedure for determination of viscosity (4.4.4.4), determine the average scale reading. Multiply this reading by 6.4 to obtain value in poises.

4.4.4.4 Determination of viscosity. Slowly pour approximately 550 ml of sample into a 600-ml Griffin beaker or other suitable container. Take care to keep trapped air at a minimum. Carefully place the spindle in the sample, again attempting to avoid air entrapment. Immerse the beaker in the constant temperature water bath to about level with the

75. 40 hours have elapsed. At the completion of 8,000 hours, capacitors shall be returned

surface of the sample, and bring the temperature of the bath to 25 ±0.1°C. Stir the sample slowly at intervals to aid in reaching the temperature equilibrium. When the temperature of the sample remains within the equilibrium range for 5 minutes, set the spindle speed of the viscometer to 5 rpm, attach the spindle to the viscometer, attach the viscometer to a support post, and center the spindle in the beaker. Adjust the spindle index mark to the surface of the sample, and take five readings of the instrument at 1-minute intervals.

Calculation:

Viscosity, 25°C, poises = f x R

where

f = ratio of stated oil viscosity (poises) to measured oil viscosity (poises)

R = average scale reading at 25°C for sample

Report the viscosity at 25°C to the nearest poise.

4.4.5 Molecular weight by gel permeation chromatography (GPC).

4.4.5.1 Apparatus.

a. Liquid chromatograph (LC), Perkin-Elmer Model 601, or equal, equipped with dual 3,000-pound force per square inch pumps, gel permeation columns, micro styragel, 1-500, 2-1,000, 1-10,000 Angstrom unit porosities, or their equal.

b. Refractometer, Perkin-Elmer Model 1107, or equal.

c. Recorder, Perkin-Elmer Model 56, with variable millivolt range, or equal.

d. Stainless pressure filter holder, Millipore Catalog Number XX30-012-00, or equal.

e. Filters, Millipore Catalog Number LSWP01300, or equal.

f. Volumetric flasks, 100-ml.

g. Syringe, 10-cubic centimeter (cm^3).

4.4.5.2 Reagents.

a. Chloroform, ACS anhydrous.

b. Standard HTPB polymer of known molecular weight distribution.

The standard is established as follows:

(1) Preparatively fraction a lot of HTPB into 8 to 10 fractions.

(2) Determine the molecular weight of each fraction by vapor pressure osmometry.

(3) Use the fractions to calibrate the GPC.

4.4.5.3 Instrument parameters.

a. LC Model 601.

(1) Solvent - chloroform

(2) Injector loop - 1 ml

(3) Oven temperature - 30°C

(4) Pump A flow rate - 1 ml/minute

(5) Pump B flow rate - 1 ml/minute

(6) Pump function - independent

(7) Pump B drain connected to refractometer reference

(8) Pump A to injector, columns, and sample side of refractometer

b. Refractometer Model 1107.

(1) Polarity - down

(2) Range - 4

(3) Circuit monitor - 0.4 to 0.6

c. Recorder Model 56.

(1) Range 5 millivolt

(2) Chart speed - 5 mm/minute

(3) Polarity - positive

4.4.5.4 Elution standard curve. Weigh accurately 0.6 gm of standard HTPB polymer into a 100-ml volumetric flask, dissolve in chloroform and dilute to volume, and mix well. Filter through the Millipore filter into a 10-cm^3 syringe and fill the loop of the LC injector. Wait 4 minutes for sample temperature to equilibrate, then inject onto the GPC columns. Using the elution curve, prepare a table of molecular weight versus elution volume as shown in Table III.

TABLE III. Elution curve example.

Molecular weight	Elution volume (counts 1/)
100,000	24.4
30,000	26.2
10,000	28.4
6,000	29.6
4,000	30.8
2,500	33.1
1,500	34.6
1,000	36.4
600	37.4
400	38.0
300	38.8

1/ One count equals 5 ml.

4.4.5.5 Determination of molecular weight. Weigh accurately 0.6 gm of sample into a 100-ml volumetric flask, dissolve in chloroform, dilute to volume, and mix well. Filter the sample solution through the Millipore filter into a 10-cm^3 syringe and fill the loop of the LC injector. Wait 4 minutes for sample temperature to equilibrate, then inject onto the GPC columns. From the chromatogram thus obtained, draw a baseline on the elution curve and measure the vertical heights from this baseline at the various molecular weight calibration points. Insert the molecular weights and corresponding heights in a computer along with the appropriate program to obtain the number average and weight average molecular weights.

Report the number average molecular weight to the nearest whole unit.

4.5 Stability. The materials shall be tested in accordance with 4.4.1, 4.4.2 and 4.4.4 after 12 months storage, and at 6-month intervals thereafter to extend the shelf life for 6-month intervals.

4.6 Examinations.

4.6.1 Inspection of filled containers. All filled containers shall be inspected prior to shipment or use for accuracy of markings and for defects in containers and closures. All defective containers and closures shall be repaired or replaced, and contents therein shall be reinspected prior to shipment or use.

4.6.2 Visual inspection. All samples shall be visually inspected to determine conformance to the requirements of 3.6.

4.6.3 Monitoring. The weighing and blending of Type I HTPB and antioxidants shall be monitored to determine compliance with 3.1 and Table I.

4.7 Records. Certification and test data shall be prepared as required by the procuring activity (see 6.2.2).

5. PACKAGING.

5.1 Packaging and packing. Unless otherwise specified in the contract or purchase order, packaging and packing of the polymers shall be in accordance with commercial practice to ensure carrier acceptance and shall be of such construction and materials that the contents will be adequately protected against loss or contamination.

5.2 Marking for shipment. Unless otherwise specified in contract or purchase order, each shipping container shall be marked in accordance with the requirements of MIL-STD-129. Container marking shall include the following:

a. The supplier's lot number.

b. Procuring activity purchase order number.

c. Container identification number (applied in numerical sequence as the containers are filled).

d. Date of manufacture.

e. Manufacturer's Code Ident.

f. Net and tare weight of the container.

g. Material identification.

h. Storage temperature limit.

6. NOTES AND CONCLUDING MATERIAL.

6.1 Intended use. The material described herein is intended to be used as an ingredient in rocket motor case liner and solid propellant formulations.

6.2 Ordering data.

6.2.1 Procurement requirements. Procurement documents should specify the following:

a. Title, number and date of this specification.

b. Responsibility for inspection and inspection facilities if different than 4.1.

c. Special packaging, packing, or shipping requirements, if applicable (see Section 5).

6.2.2 Data requirements. When this specification is used in a procurement which incorporates a Contract Data Requirements List (CDRL) (DD Form 1423) and invokes the provisions of 7-104.9(n) of the Defense Acquisition Regulations (DAR), the data requirements identified below will be developed as specified by an approved Data Item Description (DID) (DD Form 1664) and delivered in accordance with the approved DD Form 1423 incorporated into the contract. When the provisions of DAR-7-104.9(n) are not invoked, the data specified below will be delivered by the contractor in accordance with the contract requirements. Deliverable data required by this specification is cited in the following paragraphs:

Paragraph	Data Requirement	Applicable DD
4.7	Certification	UDI-A-23264B
	Test Data	DI-T-4024

(Copies of DIDs required by the contractors in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

6.3 Definitions.

6.3.1 Lot. At place of manufacture, a lot consists of one batch (see 6.3.2) or a uniform blend of two or more batches. At place of delivery, a lot consists of polymer from one supplier's lot received in a single shipment. Partial shipment may be considered as a single shipment by the procuring activity.

6.3.2 Batch. A batch consists of polymer made as one unit in an unchanged manufacturing process.

6.4 Suggested source of supply. A product that has met the requirements of this specification in past procurement actions is Atlantic Richfield Corp., Code Ident 92788, as Polymer R45M for Type I. This information is for the convenience of the procuring activity and is not to be construed as a waiver of any requirement of this specification nor as any limitation of additional potential sources of supply.

Preparing activity:
Navy - AS

(Project 6810-NB26)

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DOCUMENT IDENTIFIER *(Number)* AND TITLE

MIL-H-85497(AS), HYDROXYL-TERMINATED POLYBUTADIENE

NAME OF ORGANIZATION AND ADDRESS OF SUBMITTER

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