

MIL-L-17700(NOrd)
17 September 1953

MILITARY SPECIFICATION

LEAD SALICYLATE

1. SCOPE

1.1 Scope. - This specification covers one grade of lead salicylate intended for various military applications.

2. APPLICABLE SPECIFICATIONS, STANDARDS, AND PUBLICATIONS

2.1 The following specifications, standards, and publications, of the issue in effect on date of invitation for bids, form a part of this specification:

SPECIFICATIONS

FEDERAL

RR-S-366 - Sieves; Standard, Testing

NAVY

General Specifications for Inspection of Material

STANDARDS

MILITARY

MIL-STD-129 - Marking of Shipments

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

2.2 Other publications. - The following publication, of the issue in effect on date of invitation for bids, forms a part of this specification:

MIL-L-17700(NOrd)

Code of Federal Regulation 49CFR 71.1 -
Transportation, Interstate Commerce Commission,
Explosives and Other Dangerous Articles

(Copies of the Code of Federal Regulations may be obtained upon application, accompanied by money order, coupon, or cash, to the Superintendent of Documents, Government Printing Office, Washington 25, D.C. Prices may be obtained from the Superintendent of Documents.)

3. REQUIREMENTS

3.1 Moisture and volatiles. - Maximum, 1.0 percent.

3.2 Purity. -

3.2.1 Total lead content. - Maximum 43.7 percent; minimum, 42.2 percent.

3.2.2 Total salicylate content. - Maximum, 59.0 percent; minimum, 55.0 percent.

3.2.3 Free salicylic acid content. - Maximum, 1.0 percent.

3.3 Diethylene glycol insoluble material. - Maximum, 2.5 percent.

3.4 Color. - Cream-white to pure white.

3.5 Granulation. - Lead salicylate shall conform to the following requirement using U. S. Standard sieves conforming to Federal Specification RR-S-366, unless otherwise specified:

Retained on No. 325 0.5 percent, maximum

4. SAMPLING, INSPECTION, AND TEST PROCEDURES

4.1 Lot. - Unless otherwise specified, a lot shall consist of not more than 10,000 pounds.

4.2 Sampling. - Ten percent but in no case more than 10 or less than 3 of the containers shall be selected from each lot by the inspector so as to be representative of the lot. If there are fewer than 3 containers in the lot, all the containers shall be sampled. The material shall be thoroughly mixed and approximately 8 ounces of it shall be taken from each selected container. Each of these primary samples shall be placed in an airtight container and labelled so that the container from which

MIL-L-17700(NOrd)

it was taken can be identified. A composite sample of approximately 8 ounces shall be made from equal portions of the primary samples. The composite sample shall be thoroughly mixed and placed in an airtight container labeled to show the name of the material, manufacturer, plant, contract or order number, lot number and lot size. All acceptance tests shall be made on the composite sample. However, if it becomes apparent during sampling that the lot is not uniform, the inspector may require that any primary sample be tested for compliance with the requirements of the specification. All primary samples shall be held for possible future examination should the composite sample fail to meet the requirements.

4.3 Inspection. - Unless otherwise specified in the contract or order, inspection shall be made at the point of delivery.

4.4 Tests. -

4.4.1 Moisture and volatiles. - Transfer a portion of about 10 grams of the material to a tared glass dish about 5 cm. in diameter and about 2 cm. deep and accurately weigh the dish and contents. Place in an oven maintained at 100° to 105°C for two hours, cool in a desiccator and weigh. Calculate the loss in weight as percent moisture and volatiles.

4.4.2 Total lead content. -

4.4.2.1 Reagents. -

1. Glacial acetic acid, C.P., lead content not greater than 0.00005 percent.
2. Acetic acid, approximately 70 percent by weight obtained by diluting C.P. acetic acid with distilled water.
3. Nitric acid, C.P., lead content not greater than 0.00002 percent.
4. Sulfuric acid, C.P., lead content not greater than 0.001 percent.
5. Sulfuric acid, 3 N (about 15 percent or 1:11 dilution).
6. Ethyl alcohol, 50 percent.
7. Ethyl alcohol, 95 percent.

MIL-L-17700(NOrd)**4.4.2.2 Procedure. -**

1. Accurately weigh a 0.4000-0.4500 gram sample and transfer it to a 400- or 500-ml. tall-form beaker.
2. Add in the following order 50 ml. of 70 percent acetic acid, 20 ml. of concentrated nitric acid and 10 ml. of sulfuric acid. (Perform in a hood.)
3. Cover the beaker with a ribbed watch glass and heat on a 3-heat electric hot plate (a 7-inch diameter, 1200-Watt or an 8½-inch diameter 2000-Watt unit is satisfactory) at low heat for 20 minutes.
4. Add 10 ml. concentrated nitric acid and increase heat to medium. Continue heating until copious white fumes of sulfur trioxide appear. Use "high" heat if "medium" seems too slow when the bulk of the nitric acid has been expelled.
5. Remove the beaker from the hot plate and allow it to cool for 5-10 minutes in order to avoid spitting or too rapid evolution of gases on the addition of acid. Then add 5 ml. of concentrated nitric acid and reheat until fumes of sulfur trioxide reappear.
6. Repeat the cooling, adding nitric acid and reheating until the solution when "fumed" is colorless or very pale yellow. Then "fume" strongly for 10 minutes.
7. Remove the beaker and allow it to cool thoroughly.
8. Cautiously add 50 ml. of distilled water, washing down the cover glass and the sides of the beaker.
9. Boil the solution vigorously for 2 or 3 minutes.
10. Allow it to cool thoroughly and add about 15 ml. of 95 percent ethyl alcohol.
11. Let the solution stand at room temperature for about 2 hours.
12. Filter the solution by suction through a tared, ignited Gooch crucible with a good asbestos mat.

MIL-L-17700(NOrd)

13. Using 5 washings, of about 15-20 ml. each of 3 N sulfuric acid, carefully transfer the lead sulfate precipitate from the beaker to the crucible (this is a dense material and care is required in making a good quantitative transfer).
14. Continue washing the lead sulfate in the Gooch crucible. Use 2 washes with 50 percent alcohol and one with 95 percent alcohol.
15. Dry the crucible by suction for about 5 minutes and then complete the drying in an oven for 15-30 minutes at 105-110°C.
16. Ignite the crucible in a furnace at 500-600°C for 15 minutes. (Alternatively, ignition may be accomplished by placing the Gooch crucible inside a large porcelain crucible which is directly fired in the full blast of a Fisher burner. With this type of equipment, ignite for 5 minutes. The usual crucible used is a Coors No. 3.)
17. Cool the Gooch crucible in a desiccator and reweigh.
18. Calculate the percent total lead by multiplying the weight of lead sulfate obtained by 68.32 and dividing by the weight of sample used. The mean of duplicate determinations shall be reported.

4.4.3 Total salicylate content. -

4.4.3.1 Apparatus. -

1. A Beckman Model DU Spectrophotometer or a Bausch and Lomb Photoelectric Colorimeter using filter 505 millimicrons ($m\mu$), or an equivalent photometer.
2. Volumetric flasks, 1 liter, 200 ml., 25 ml., and an assortment of pipets 5 ml., 10 ml., 20 ml.
3. A pH meter.

MIL-L-17700(NOrd)

4.4.3.2 Reagents. -

1. Acetic acid, glacial C.P.
2. Acetic acid, 6 percent; prepared by diluting 60 ml. of C.P. glacial acetic acid with 940 ml. of distilled water.
3. Weak acetic acid, prepared by diluting 13 ml. of C.P. glacial acid to 1 liter with distilled water. The pH of this solution should be approximately 2.7. If it is outside the range 2.6-2.8 adjustment of the pH should be made by adding acetic acid or potassium hydroxide solution to arrive at pH 2.7.
4. Ferric alum solution, prepared as follows:
Dissolve 6 grams of C.P. ferric ammonium sulfate, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, in 50 ml. of water, add 0.1 ml. of 30 percent hydrogen peroxide, and boil until the peroxide is destroyed (2 minutes). Add 5 ml. of 1:1 sulfuric acid solution and heat until the solution is clear. Cool, dilute to 90 ml. with water, and adjust to a pH of 1.4 with 10 percent potassium hydroxide solution, using a pH meter, and finally dilute to 100 ml. This solution will last indefinitely when stored in a glass stoppered flask.
5. Sodium salicylate C.P. (alternatively C.P. salicylic acid may be used).

4.4.3.3 Standard Curve. - Prepare a standard solution of salicylate as follows: Add exactly 0.2000 grams of sodium salicylate to about 900 ml. water in a beaker, then regulate the pH to 2.7 by the addition of 6 percent acetic acid. Finally transfer to a 1 liter volumetric flask and dilute to the mark with distilled water. Establish points for the calibration curve by withdrawing aliquots of 1 ml., 2 ml., 4 ml., 5 ml., and 6 ml. Place each of the aliquots in a 25 ml. volumetric flask, add 0.25 ml. of the ferric alum solution and dilute to the mark with the weak acetic acid (pH 2.7) solution. Allow 5 minutes for full color development. Obtain absorbance readings of these solutions against a ferric alum blank. The blank is made up exactly the same as the solutions above but without adding salicylate. Wave length 520 μ is used for all absorbance readings. The concentration scale is most conveniently plotted in terms of salicylate, using the data of column 3 of the following table:

MIL-L-17700(NOrd)

SUMMARY OF CALIBRATION DATA

<u>Salicylate Standard Solution ml</u>	<u>mg Na Sal Present in 25 ml</u>	<u>Theoretical Salicylate Equivalence mg per 25 ml</u>	<u>Absorbance Values</u>
1	0.2	0.17	To be determined
2	0.4	0.34	To be determined
4	0.8	0.68	To be determined
5	1.0	0.85	To be determined
6	1.2	1.03	To be determined

From the standard graph a table can be prepared for routine work giving percent total salicylate readings corresponding to small increments of absorbance when the prescribed weight of sample and size of aliquots have been employed.

4.4.3.4 Procedure. -

1. Accurately weigh a 0.3000 gram sample and transfer it to a 1 liter volumetric flask. Add 25 ml. of glacial acetic acid, measured with a pipet, and swirl the mixture to facilitate dissolution of the material. When the sample is in solution (it may be slightly cloudy at this point) the solution is diluted to volume with distilled water.
2. When the solution is thoroughly mixed withdraw 10 ml. aliquots and transfer to 50 ml. volumetric flasks. Add 0.50 ml. of the ferric alum solution and dilute to volume with the weak acetic acid (pH 2.7) solution. Transfer the colored solution to a 1 cm. cell of the Beckman spectrophotometer or to the cell of the photoelectric colorimeter. Prepare a blank for spectrophotometric comparison by transferring 0.50 ml. of the ferric alum solution to a 50 ml. volumetric flask and diluting to volume with the weak acetic acid (pH 2.7) solution. Make absorbance readings at 520 μ on the Beckman spectrophotometer. When a filter instrument is used, the filter transmitting in the 500-550 μ range is selected for use.
3. The quantity of salicylate present is read from the standard graph and the percent total salicylate in the material calculated.

MIL-L-17700(NOrd)

4.4.4 Free salicylic acid content. -4.4.4.1 Apparatus. -

1. A Beckman Model DU Spectrophotometer with ultra-violet source and 1 cm. silica cells.
2. Filter paper, Whatman No. 1.
3. 60° filter funnels.
4. Volumetric flasks, 1 liter, 100 ml., 50 ml. and 10 ml. pipets.
5. Beakers, low form, 250 ml.

4.4.4.2 Reagents. -

1. Chloroform, C.P. CHCl_3 .
2. Salicylic acid, C.P.

4.4.4.3 Standard curve. - The standard curve may be made most easily by dissolving a known amount of C.P. salicylic acid in C.P. chloroform and making readings on known dilutions of this solution with C.P. chloroform in the reference cell. For example, 100 mg of salicylic acid dissolved in 1000 ml. of chloroform will serve as a strong stock solution from which the following dilutions may be prepared.

	<u>ml. of Stock Solution</u>	<u>Made Up in CHCl_3 to ml.³</u>	<u>mg. Sal. Acid per 100 ml. Dilute Solution</u>
(a)	50 strong stock	100	5
(b)	25 " "	100	2.5
(c)	20 " "	100	2.0
(d)	15 " "	100	1.5
(e)	10 " "	100	1.0
(f)	25 ml. of solution (d)	50	0.75
(g)	25 " " " (e)	50	0.50
(h)	10 " " " (b)	100	0.25

Readings are all taken at 310 μ using a slit width chosen for best sensitivity (a slit width of 0.22 was used in developing the procedure). The plot should give a straight line passing through the origin.

MIL-L-17700(NOrd)

4.4.4.4 Procedure. -

1. Accurately weigh a 1.000 g. of sample and transfer to a 250 ml. beaker. Add 80 ml. of chloroform and warm on a hot plate set at "low" for 20-30 minutes with occasional agitation to insure complete extraction. Cool to room temperature and filter through a Whatman No. 1 filter paper into a 100 ml. volumetric flask. Rinse the beaker and residue twice with 5-10 ml. portions of chloroform, pouring the rinsings through the filter into the volumetric flask. Dilute the solution to volume with chloroform and mix well. Transfer a 10 ml. aliquot to a 50 ml. volumetric flask. Make up to volume with chloroform and mix well.
2. Determine the absorbance of the diluted solution with the Beckman DU spectrophotometer at 310 μ , using chloroform in the reference cell. Calculate the percent free salicylic acid in the sample. For absorbance readings the limits 0.2 to 0.8 are usually considered satisfactory. If the specified dilution makes a solution which has absorbance outside the desired range a suitable dilution of the original solution should be used. If the specified weight of sample and dilutions are used, the percent free salicylic acid would be calculated as follows: mg. salicylic acid read from graph multiplied by 500.

4.4.5 Diethylene glycol insoluble material. - Transfer exactly 2.000 g. of the material to a suitable flask or large test tube and add 18.0 ml. of C.P. diethylene glycol. Mix well and immerse the test tube in a water bath held at $70^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 30 minutes. Filter while hot through a tared medium porosity pyrex crucible using suction. Rinse the test tube three times with 5 ml. portions of diethylene glycol heated to 70°C pouring the rinsings through the crucible. Wash the crucible contents twice with 5 ml. portions of 95 percent ethanol and aspirate to air dry the residue. Place the crucible and contents in a 110°C oven for one hour, cool in a desiccator and weigh. The weight of residue multiplied by 50 will give the percent insoluble in diethylene glycol.

4.4.6 Color. - Determine the color of the sample by visual inspection.

MIL-L-17700(NOrd)

4.4.7 Granulation. - Transfer a weighed portion of 10 gm. of the sample to a 600 ml. beaker and wet thoroughly with 95-percent ethyl alcohol, breaking up all lumps with a stirring rod. Add to the beaker about 500 ml. of a 1:1 water-alcohol mixture and stir vigorously to suspend the solid material in the liquid. Pour the suspension on a tared 3 inch, No. 325 U. S. Standard sieve, discarding the material going through the sieve. Wash any of the sample remaining in the beaker on the sieve by means of a stream of 1:1 water-alcohol mixture. Wash the residue on the sieve by brushing and washing with 1:1 alcohol-water mixture until the washings come through with only a slight turbidity. Rinse the sieve once with 95-percent ethyl alcohol and then air-dry the sieve. Place the sieve in an oven at 100° to 105° for one-half hour, cool in a desiccator and weigh. Calculate the gain in weight of the sieve to percent lead salicylate retained on the sieve.

5. PREPARATION FOR DELIVERY

5.1 Packaging and packing. - Unless otherwise specified lead salicylate shall be packaged and packed in substantial commercial containers so constructed as to insure acceptance by common or other carrier for safe transportation at the lowest rate to the point of delivery.

5.2 Marking. - In addition to any special marking required by the contract or order, shipments shall be marked in accordance with Standard MIL-STD-129. Each container shall be labeled "Lead Salicylate" and all markings shall conform with the applicable regulations of the Interstate Commerce Commission.

6. NOTES

6.1 Ordering Data. - Invitations for bids and contracts or orders should specify the number, the date, and the title of the specification.

Notice. - When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.