

INCH-POUND

MIL-DTL-46110C
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SUPERSEDING
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DETAIL SPECIFICATION

COATING COMPOUND, OXIDE BLACK

Reactivated after 30 December 2009 and may be used for new and existing designs and acquisitions.

This specification is approved for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers one grade of a coating compound for use in blackening ferrous metals to conform to MIL-DTL-13924, class 1 (for wrought iron, plain carbon, and low alloy steels).

2. APPLICABLE DOCUMENTS

2.1 General. The documents listed in this section are specified in sections 3 and 4 of this specification. This section does not include documents cited in other sections of this specification or recommended for additional information or as examples. While every effort has been made to ensure the completeness of this list, document users are cautioned that they must meet all specified requirements of the documents cited in sections 3 and 4 of this specification, whether or not they are listed.

2.2 Government documents.

2.2.1 Specifications. The following specification forms a part of this document to the extent specified herein. Unless otherwise specified, the issues of this document are those cited in the solicitation or contract.

Comments, suggestions, or questions on this document should be addressed to Defense Supply Center Richmond, ATTN: DSCR-VEB, 8000 Jefferson Davis Highway, Richmond, VA 23297-5616, or e-mailed to STDZNMGT@dla.mil. Since contact information can change, you may want to verify the currency of this address information using the ASSIST database at <https://assist.daps.dla.mil/>.

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DEPARTMENT OF DEFENSE SPECIFICATION

MIL-DTL-13924 - Coating, Oxide, Black, for Ferrous Metals

(Copies of this document are available online at <https://assist.daps.dla.mil/> or from the Standardization Document Order Desk, 700 Robbins Avenue, Building 4D, Philadelphia, PA 19111-5094.)

2.3 Non-government publications. The following document forms a part of this document to the extent specified herein. Unless otherwise specified, the issues of this document are those cited in the solicitation or contract.

AMERICAN SOCIETY FOR QUALITY (ASQ)

ASQ Z1.4 - Sampling Procedures and Tables for Inspection by Attributes

(Copies of this document are available from <http://www.asq.org/> or American Society of Quality, 600 North Plankinton Avenue, Milwaukee, WI 53203.)

2.4 Order of precedence. Unless otherwise noted herein or in the contract, in the event of a conflict between the text of this document and the references cited herein, the text of this document takes precedence. Nothing in this document, however, supersedes applicable laws and regulations unless a specific exemption has been obtained.

3. REQUIREMENTS

3.1 Material. The coating compound shall consist of ground flake or granular sodium hydroxide (NaOH) and granular or bead sodium nitrate (NaNO₃) intimately blended together as a coarse, dust-free material. The coating compound shall contain no added sulfur compounds, other than those present in the basic chemical ingredients. The particle size shall not be greater than 6.35 millimeter (mm) (0.25 inch) maximum for any dimension when examined visually. The coating compound shall be capable of producing a black oxide coating meeting the requirements of MIL-DTL-13924, class 1.

3.2 Color. The mixture shall have a white or pale yellow color when examined in accordance with 4.3.3.

3.3 Chemical requirements. The mixture shall conform to the applicable chemical requirements specified in table I when tested as specified in the corresponding test paragraphs in section 4.

3.4 Workmanship. The material shall be processed in a manner that will produce a uniform mixture when examined visually (see 4.3.3).

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TABLE I. Chemical requirements.

Property	Percentage	Test method
Moisture	0.5 max	4.3.4
Insoluble matter	0.5 max	4.3.5
Chlorates (as NaClO ₃)	0.06 max	4.3.6
Chlorides (as NaCl)	1.0 max	4.3.7
Sodium hydroxide (as NaOH)	63.0 min	4.3.9
Carbonate (as Na ₂ CO ₃)	1.3 max	4.3.10
Total alkalinity (as Na ₂ O)	48.8 min	4.3.11
Sodium nitrate (as NaNO ₃)	33.0 min	4.3.12
Calcium oxide (as CaO)	0.1 max	4.3.13
Magnesium (as MgO)	0.1 max	4.3.14
Sulfates (as Na ₂ SO ₄)	0.5 max	4.3.15

4. VERIFICATION

4.1 Conformance inspection. Conformance of the material to the requirements of this specification shall consist of an examination for acceptability of quality control methods used by the manufacturer, examining and testing the acceptance samples (see 4.2.3) for all the requirements.

4.2 Sampling.

4.2.1 Inspection lot. A lot shall consist of the material produced by one manufacturer under essentially the same manufacturing conditions with no change in materials and provided the operation is continuous. In the event that the process is a batch operation, each batch shall constitute a lot (see 6.3).

4.2.2 Nondestructive examination. Sampling shall be conducted in accordance with ASQ Z1.4, inspection level II, with the Acceptance Quality limit (AQL) as specified in the contract (see 6.2).

4.2.3 Sample of tests. Three separate 0.454 kilograms (kg) (1-pound) samples shall be taken from each inspection lot. When the material is produced by a batch process the three samples shall be taken at different locations within each batch or from three separate containers. When the material is produced by a continuous-run process the three samples shall be taken so as to represent, respectively, the first part, the middle part, and the last part of the run of the constituted inspection lot. The individual specimens shall be tested as specified in 4.3.

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4.2.4 Examination of filled containers. A sample of filled containers shall be taken at random in accordance with ASQ Z1.4, inspection level II, with the AQL as specified in the contract (see 6.2), checked for defects listed in 4.2.5.

4.2.5 Classification of defects. The classification of defects with respect to preparation for delivery (see section 5) is as follows.

4.2.5.1 Critical classifications. No items are classified as critical.

4.2.5.2 Major classifications. The following items are classified as major.

Major:

101	Unit of shipping container not as specified.
102	Quantity of material per unit or shipping container not as specified.
103	Closure of unit or shipping container not as specified.
104	Unit or shipping container damaged.
105	Evidence of sifting or leakage.
106	Marking of unit or shipping container, illegible, incorrect, or incomplete.

4.3 Inspection methods. Unless otherwise specified, the chemical values in table I shall apply to the average of the determinations made on the product.

4.3.1 Mixture conformance. Conformance of the mixture to the requirements for material (see 3.1) and workmanship (see 3.4) shall be determined by processing 50 mm x 100 mm x 3 mm (2" x 4" x 1/8") panels of low carbon steel, cold rolled, in a prepared aqueous solution (approximately 1079 grams per liter (g/l) (9 pounds per gallon)) operated at a rolling boil at 140 to 152 °C (284 to 305 °F) for a period of 30 minutes, maximum. The panels shall be examined and tested for compliance of the black oxide coating with class 1 of MIL-DTL-13924.

Note: For safety, the procedure described in 4.3.1 should be performed in a metal container.

4.3.2 Tests. Distilled water and analytical reagent grade chemicals shall be used throughout the tests. Where applicable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.3.3 Color and form. The composite and individual specimens shall be visually examined for compliance with 3.2 and 3.4.

4.3.4 Moisture (see 6.4). Transfer a weighed 10 gram (g) portion of the mixture to a previously tared shallow weighing bottle, heat in a convection oven for 2 hours at 150 ±3 °C (302 ±5 °F), cover, cool in a desiccator and weigh. Calculate the loss in weight as the percentage of moisture in the sample.

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$$\text{Percent moisture} = \frac{100 \times (A - B)}{W}$$

where:

- A = Weight of bottle plus sample before drying in grams.
- B = Weight of bottle plus sample after drying in grams.
- W = Weight of sample in grams.

4.3.5 Insoluble matter. Transfer a weighed 25 g sample of the mixture to a beaker. Heat to boiling with 200 milliliters (ml) of distilled water and decant the solution through a filtering crucible of fine porosity having a nominal maximum pore diameter of 4.5 to 5 micrometers (microns) which has been dried at 105 ± 5 °C (221 ± 9 °F) and weighed. Rinse the beaker with boiling distilled water and transfer any adhering insoluble matter to the filter. Decant the wash water from the beaker through the filter. The filtering crucible shall be dried in an oven at 105 ± 5 °C (221 ± 9 °F) for 3 hours, cooled in a desiccator and weighed. The increase in weight shall be calculated as percent insoluble matter as follows:

$$\text{Percent insoluble matter} = \frac{100 \times (A - B)}{W}$$

where:

- A = Weight of crucible plus residue in grams.
- B = Weight of crucible in grams.
- W = Weight of sample in grams.

4.3.6 Chlorates. Transfer a weighed 25 g sample of the dried mixture to a beaker and dissolve in hot distilled water. Add sufficient nitric acid (HNO_3) to make the solution acid to litmus and then add 5 ml of nitric acid and an excess of silver nitrate (AgNO_3) solution and stir. Filter the solution to remove any chlorides that may have been precipitated. Add to the solution 10 ml of 30 percent formaldehyde solution and heat on the water bath for 30 minutes. Chlorate is thus reduced to chloride and precipitated by the excess silver nitrate. Filter off the precipitate on a tared filtering crucible of fine porosity having nominal maximum pore diameter of 4.5 to 5 microns, which has previously been dried at 105 ± 5 °C (221 ± 9 °F). Dry the crucible and precipitate for 3 hours at 105 ± 5 °C (221 ± 9 °F). Cool in a desiccator and weigh. Calculate the percentage of sodium chlorate (NaClO_3) as follows:

$$\text{Percent sodium chlorate} = \frac{74.3 \times A}{W}$$

where:

- A = Weight of precipitate in grams.
- W = Weight of sample in grams.

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4.3.7 Chlorides. Carefully weigh a 25 g dried sample of the mixture and transfer it to a 600 ml beaker. The sample shall be dissolved in 300 ml of hot (approximately 85 °C (185 °F)) distilled water and 35 ml of concentrated nitric acid added. Add 25 ml of approximately 0.1 N silver nitrate solution to the solution with the aid of a pipette. The precipitate shall be heated to boiling on a hot plate with occasional stirring, and boiled moderately for approximately 2 minutes with constant stirring. The beaker and contents shall be removed from the hot plate. The precipitate shall be allowed to settle (if the precipitate does not settle rapidly it is permissible to filter the solution as specified and test the filtrate) and one drop of the supernatant liquid shall be added to one drop of a one percent solution of sodium chloride (NaCl) on a black porcelain spot plate. If no precipitate occurs on the spot plate, a second 25 ml portion of silver nitrate solution shall be added to the sample, boiled as indicated above, and the spot test repeated. The addition of silver nitrate solution shall be continued and the spot test repeated as specified above until a precipitate of silver chloride (AgCl) is obtained. The supernatant solution shall be filtered through a tared Pyrex sintered glass crucible of fine porosity, having a nominal maximum pore diameter of 4.5 to 5 microns, and with the aid of suction, the filtrate shall be collected in a 1000 ml filtering flask. The silver chloride precipitate shall be transferred quantitatively to the filtering crucible with the aid of five 20 ml portions of 1:100 nitric acid solution and one 20 ml portion of distilled water. The crucible and contents shall be dried in an oven at 105 ± 5 °C (221 ± 9 °F) for 3 hours. The crucible shall be cooled in a desiccator and weighed. The percent chlorides, as sodium chloride in the sample, shall be calculated as follows:

$$\text{Percent sodium chloride} = \frac{40.8 \times (A - B)}{W}$$

where:

- A = Weight of crucible plus precipitate in grams.
- B = Weight of crucible grams.
- W = Weight of sample in grams.

4.3.8 Preparation of solutions.

4.3.8.1 Barium chloride solution. Dissolve 10 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in freshly boiled and cooled distilled water and dilute to 100 milliliters. Use this solution in 4.3.9 and 4.3.15.

4.3.8.2 Sample test solution. Weigh quickly to the nearest milligram into a glass-stoppered weighing bottle approximately 30 g of the sample material (see 6.4). Transfer the weighed material to a 1-liter volumetric flask, rinsing the bottle several times with water to assure complete transfer of the material. Add sufficient freshly boiled and cooled water to half fill the flask and agitate the contents until all solid material is dissolved. Cool to room temperature and dilute with water to mark. Save this test solution for determinations 4.3.9, 4.3.12, 4.3.13, and 4.3.15. Use the above sample weight as S in calculations of 4.3.9 through 4.3.15.

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4.3.9 Sodium hydroxide. Pipette 50.0 ml of test solution (see 4.3.8.2) into a 250 ml Erlenmeyer flask, add 25 ml of a neutral 10 percent aqueous solution of barium chloride (see 4.3.8.1), and titrate with 0.5 *N* hydrochloric acid (HCl), using 3 drops of phenolphthalein (C₂₀H₁₄O₄) solution, to disappearance of the pink color. Save this solution for the carbonate determination in 4.3.10. Calculate the percent sodium hydroxide as follows:

$$\text{Percent sodium hydroxide} = \frac{80 \times V \times N}{S}$$

where:

- V = Volume of hydrochloric acid solution used in ml.
- N = Normality of hydrochloric acid solution used.
- S = Weight of specimen used in grams (see 4.3.8.2).

4.3.10 Carbonate. Add 2 drops of methyl orange indicator to the solution reserved from the sodium hydroxide assay (see 4.3.9) and titrate with 0.1 *N* hydrochloric acid solution to a pink color, which persists for one minute. Calculate the percent of carbonate as sodium carbonate (Na₂CO₃) as follows:

$$\text{Percent carbonate} = \frac{212 \times B \times M}{S}$$

where:

- B = Volume of hydrochloric acid solution used in ml.
- M = Normality of hydrochloric acid solution used.
- S = Weight of specimen used in grams (see 4.3.8.2).

4.3.11 Total alkalinity. Calculate the total alkalinity (Na₂O) as follows:

$$\text{Percent total alkalinity} = \frac{62 \times (V \times N + B \times M)}{S}$$

where:

- V = Volume of hydrochloric acid solution used in 4.3.9 in ml.
- N = Normality of hydrochloric acid solution used in 4.3.9.
- B = Volume of hydrochloric acid solution used in 4.3.10 in ml.
- M = Normality of hydrochloric acid solution used in 4.3.10.
- S = Weight of specimen used in grams (see 4.3.8.2).

4.3.12 Sodium nitrate. Pipette 5 ml of the test solution (see 4.3.8.2) into a 250 ml beaker. Add 100 ml of distilled water and 2.0 ml of 6 *N* sulfuric acid (H₂SO₄). Heat to boiling, and add 10 ml of nitron reagent (10 g of nitron in 100 ml of 50 percent glacial acetic acid (CH₃COOH)). Keep in a dark colored bottle). Cool and place in an ice-bath for 1.5 hours. Filter

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through a weighed, fritted glass crucible of medium porosity, having a nominal maximum pore diameter of 10 to 15 microns, and place a piece of ice in the crucible before filtering. The solution must be cooled to reduce the solubility of the nitron compound. Use the filtrate to effect transfer of all the precipitate. Wash the collected precipitate in the crucible with four 3 ml portions of ice water. Reboil the filtrate, and add a small quantity of nitron reagent to check the completeness of the precipitation. Dry the crucible at 105 ± 5 °C (221 ± 9 °F). Cool in a desiccator, and weigh. Repeat the weighing procedure until a constant weight is obtained. Calculate the percent sodium nitrate as follows:

$$\text{Percent sodium nitrate} = \frac{4530 \times A}{S}$$

where:

- A = Weight of precipitate in grams.
S = Weight of specimen used in grams (see 4.3.8.2).

4.3.13 Calcium oxide. By means of pipette, transfer to an Erlenmeyer flask or beaker 100 ml of the test solution prepared as specified in 4.3.8.2. Make distinctly acid with 5 ml of concentrated nitric acid. Then make distinctly alkaline with ammonium hydroxide (NH₄OH) and heat to boiling. Precipitate the calcium by adding 10 ml of a saturated solution of ammonium oxalate ((NH₄)₂C₂O₄ · H₂O). Continue the boiling for 5 to 10 minutes, until the small bubbles from the reaction cease, filter the precipitate on #42 Whatman paper or equivalent, wash off solids with cold distilled water containing 5 percent ammonium hydroxide, and determine the percentage of calcium oxide either gravimetrically or volumetrically. Save the filtrate for the magnesium determination in 4.3.14.

Note: The glassware used for the procedure described in 4.3.13 should also be rinsed following the procedure, using the 5 percent ammonium hydroxide solution, to remove solids.

4.3.13.1 Volumetric determination. Wash the filter paper and precipitate thoroughly and then transfer paper and precipitate to a beaker containing 400 ml hot water to which has been added 10 ml of 18 N sulfuric acid. Disintegrate the paper by stirring vigorously with a glass rod and then titrate rapidly while hot with approximately 0.05 N potassium permanganate (KMnO₄) solution until a pink endpoint persists for 30 seconds. Calculate the percentage of calcium oxide as follows:

$$\text{Percent of calcium oxide} = \frac{28 \times V \times N}{S}$$

where:

- V = ml of potassium permanganate solution used.
N = Normality of potassium permanganate solution.
S = Weight of sample in grams (see 4.3.8.2).

This method is preferred for small amounts of calcium oxide since it is more accurate.

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4.3.13.2 Gravimetric determination. The precipitate and filter paper is placed in a weighed crucible and gently heated, the crucible being covered, until the water is expelled and the paper charred. Do not let paper burn or let flame occur. Transfer to a muffle furnace and heat to 1200 °C (2192 °F) for 5 to 10 minutes. It is well to remove the cover for an instant to assist escape of the carbon dioxide (CO₂) during the heating. The covered crucible and its contents are cooled in a desiccator containing concentrated sulfuric acid. The cooled calcium oxide (CaO) is weighed and the ignition repeated until the weight is constant. Calculate the percentage of calcium oxide as follows:

$$\text{Percent of calcium oxide} = \frac{1000 \times (A - B)}{S}$$

where:

- A = Weight of crucible plus residue in grams.
- B = Weight of crucible in grams.
- S = Weight of sample in grams (see 4.3.8.2).

This method is preferred for percentages of calcium oxide near the maximum.

4.3.14 Magnesium. Catch the filtrate and wash water from the calcium oxide determination (4.3.13) in a beaker. Add 10 ml of a 10 percent solution of disodium phosphate (Na₂HPO₄) and then a volume of concentrated aqueous ammonia (27 to 30 percent) equal to approximately 10 percent of the volume of liquid in beaker. Mix thoroughly and allow to stand overnight. Filter the precipitate on #42 Whatman filter paper or equivalent, wash with 5 percent aqueous ammonia and ignite in a tared platinum crucible. If the ignition does not result in a white precipitate, cool the crucible and contents, add a few drops of nitric acid or ammonium nitrate (NH₄NO₃) solution, heat gradually and then ignite fully. Spattering must be avoided. Cool in a desiccator and weigh. Calculate the percentage of magnesium oxide (MgO) as follows:

$$\text{Percent magnesium oxide} = \frac{362 \times (A - B)}{S}$$

where:

- A = Weight of precipitate plus crucible in grams.
- B = Weight of crucible in grams.
- S = Weight of sample in grams (see 4.3.8.2).

4.3.15 Sulfates. By means of a pipette transfer to a beaker 200 ml of the test solution prepared as specified in 4.3.8.2. Add sufficient hydrochloric acid to make the solution slightly acid, and heat to boiling. Slowly add 10 ml of a 10 percent solution of barium chloride dihydrate (see 4.3.8.1) and heat to boiling. Settle the precipitate on a steam bath and then filter in a tared filtering crucible of fine porosity having a nominal maximum pore diameter of 4.5 to 5 microns. Calculate the percentage of sodium sulfate (Na₂SO₄) as follows:

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$$\text{Percent sodium sulfate} = \frac{304.5 \times (A - B)}{S}$$

where:

- A = Weight of precipitate plus crucible in grams.
- B = Weight of crucible in grams.
- S = Weight of sample in grams (see 4.3.8.2).

4.3.16 Acceptance and rejection criteria. If the individual or composite sample fails to meet the test requirements of the specification, the lot shall be rejected. When rejected lots of the material are submitted for acceptance inspection, samples shall be selected in accordance with the provisions of ASQ Z1.4, inspection level II, with the AQL as specified in the contract (see 6.2), employing tightened inspection.

5. PACKAGING

5.1 Packaging. For acquisition purposes, the packaging requirements shall be as specified in the contract or order (see 6.2). When packaging of materiel is to be performed by DoD or in-house contractor personnel, these personnel need to contact the responsible packaging activity to ascertain packaging requirements. Packaging requirements are maintained by the Inventory Control Point's packaging activities within the Military Service or Defense Agency, or within the military service's system commands. Packaging data retrieval is available from the managing Military Department's or Defense Agency's automated packaging files, CD-ROM products, or by contacting the responsible packaging activity.

6. NOTES

(This section contains information of a general or explanatory nature that may be helpful, but is not mandatory.)

6.1 Intended use. The material covered by this specification is intended for use in blackening wrought iron, plain carbon, and low alloy steels, listed as class 1 of MIL-DTL-13924. Information on procedures for blackening steel including concentration of solution, temperature of solution, and time of immersions are noted in MIL-HDBK-205.

6.2 Acquisition requirements. Acquisition documents should specify the following:

- a. Title, number, and date of this specification.
- b. Container capacity required.
- c. AQL (see 4.2.2, 4.2.4, and 4.3.16).
- d. Packaging requirements (see 5.1).

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process and subjected to some physical operation intended to make the final product substantially uniform.

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6.4 Avoid contact with air. This material rapidly deliquesces in air and absorbs carbon dioxide. Contact with air must be avoided as much as possible in order to eliminate errors in analysis.

6.5 Subject term (key word) listing.

Wrought iron
Plain carbon
Low alloy steels

6.6 Changes from previous issue. Marginal notations are not used in this revision to identify changes with respect to the previous issue due to the extent of the changes.

Custodians:

Army - CR
Navy - SH
Air Force - 68
DLA - GS

Preparing Activity:

DLA - GS3

(Project 6850-2009-011)

Review Activities:

Army - SM
Navy - MC, OS

NOTE: The activities listed above were interested in this document as of the date of this document. Since organizations and responsibilities can change, you should verify the currency of the information above using the ASSIST database at <https://assist.daps.dla.mil/>.