MIL-C-13924C
9 June 1980
SUPERSEDING
MIL-C-13924B
30 March 1966

MILITARY SPECIFICATION

COATING, OXIDE, BLACK, FOR FERROUS METALS

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

1. SCOPE

1.1 Scope. This specification covers black oxide coatings applied to ferrous metals (wrought iron, carbon, low alloy, and corrosion resistant steels). Black oxide coatings, with or without a supplementary preservative treatment (see 3.11), may be used where a black surface is required. Only very limited corrosion protection, under mildly corrosive conditions, is obtained as a result of black oxide coating (see 6.1). Black coatings are included in this specification with limitations as noted in 1.2.

1.2 Classification. Black oxide coatings covered by this specification shall be of the following classes as specified (see 6.4).

Class 1 - Alkaline oxidizing process (for wrought iron, cast and malleable irons, plain carbon, and low alloy steels).

Class 3 - Fused salt oxidizing process (for corrosion resistant steel alloys which are tempered at 900 F (482 C) or higher).

Class 4 - Alkaline oxidizing process (for 300 series corrosion resistant steel alloys only).

2. APPLICABLE DOCUMENTS

2.1 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.

/ Area MFFP /

Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Director, US Army Materials and Mechanics Research Center, ATTN: DRXMR-LS, Watertown, MA 02172 by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

SPECIFICATIONS

FEDERAL

TT-C-490 - Cleaning Method and Pretreatment of Ferrous Surfaces for Organic Coatings

VV-L-800 - Lubricating Oil, General Purpose, Preservative, (Water-Displacing, Low Temperature)

MILITARY

MIL-S-5002 - Surface Treatments and Inorganic Coatings for Metal Surfaces of Weapons Systems

MIL-C-16173 - Corrosion Preventive Compound, Solvent Cutback, Cold-Application

DOD-P-16232 - Phosphate Coating, Heavy, Manganese or Zinc Base (For Ferrous Metals)

STANDARDS

MILITARY

MIL-STD-105 - Sampling Procedures and Tables for Inspection by Attributes

HANDBOOKS

MILITARY

MIL-HDBK-205 - Phosphating and Black Oxide Coating of Ferrous Metals

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

2.2 Other publications. The following document forms a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) STANDARDS

B 117 - Method of Salt Spray (Fog) Testing

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

3. REQUIREMENTS

3.1 Materials. The materials for the blackening processes shall be selected by the contractor. The selected materials shall result in black coatings meeting all the applicable requirements of this specification.

3.2 Preparation of basis metal. Prior to the application of the black coatings, the basis metal shall be thoroughly cleaned as prescribed in MIL-S-5002. Cleaning materials and methods shall be at the option of the contractor. The cleaning process shall be performed without measurable abrasion or erosion. The cleaned surfaces shall be free of rust, scale, grease, oil, paint, or other foreign matter.

3.2.1 Stress relief treatment. All parts which are cold formed or which contain residual tensile stress, such as may be produced by cold straightening, shall be given a stress relief treatment in accordance with MIL-S-5002 before cleaning and coating.

3.2.2 Coating as a final process. Unless otherwise specified, the black coatings shall be applied after all machining, forming, welding, cold straightening and heat treatment have been completed.

3.3 Application of black coatings. The coating shall conform to the class specified. The specified black coating shall be applied under controlled time and temperature conditions. All equipment together with solutions or baths shall be properly maintained and kept free of dirt or possible contaminants. The selected process shall not reduce the hardness of the parts being processed or expose the parts to temperatures in the temper brittle range of the material, nor shall it cause embrittlement of the steel.

3.3.1 Surface attack. The process shall not result in any attack of the surface, either pitting or intergranular. Daily determination for this behavior shall be made using a microscopic method and examined at a magnification which will clearly establish the condition. Parts with pitted surfaces or showing intergranular attack shall be rejected.

3.4 Alkaline oxidizing solutions (class 1). Class 1 oxide coatings shall be formed from a boiling alkaline-oxidizing solution.

3.4.1 Rinsing. Class 1 black oxide coated pieces shall be rinsed immediately after processing in a stagnant warm rinse at 140 to 190 F (60 to 88 C) followed by thorough cold water rinsing to effect complete removal of blackening solution.

3.4.2 Chromic acid dip. After the cold water rinse (see 3.4.1) the pieces shall be dipped for a minimum of 30 seconds in a 0.06 percent solution (8 oz. chromic acid per 100 gallons water) of chromic acid maintained at a temperature of 150 to 190 F (66 to 88 C) and a pH of 2 to 3. After the chromic acid dip, parts shall be dried without further rinsing by using warm dry air.

3.5 Fused salt oxidizing (class 3). The temperature of the molten oxidizing salt of class 3 shall not be higher than 900 F (482 C). After suitable immersion, the treated parts shall be withdrawn, cooled from eight to ten minutes and rinsed in hot water, 190 F (88 C), followed by thorough cold water rinsing to effect complete removal of blackening solution. After rinsing, the parts shall be dried by warm dry air and given a chromic acid dip as outlined in 3.4.2.

3.6 Alkaline oxidizing (class 4). The black coating of class 4 shall be processed in accordance with instructions furnished by the suppliers of the raw materials and the resulting coating shall conform to the applicable requirements of this specification.

3.7 Coverage and color. The class 1, 3, and 4 coatings (see 1.2) shall cover the basis metal completely and shall pass the smut test. The color shall be a uniform black. A slight amount of smut, which is inherent in the process, shall not be cause for rejection. There shall be no indication of any reddish-brown or green smut when tested as in 4.4.1. Smut "spottiness" shall be classified as unsatisfactory requiring reprocessing.

3.8 Quality coating (oxalic acid spot test for classes 1 and 3). The black oxide coatings of classes 1 and 3, prior to the application of a preservative, shall pass the oxalic acid spot test for a good quality coating (figure 3) as specified in 4.4.2.

3.9 Resistance to salt spray (fog) (class 4 AISI Type 300 series corrosion resistant steel only). The black coating, of class 4 (300 series only), prior to the application of a prservative, shall show no signs of corrosion after 96 hours of exposure in the salt spray test (see 4.4.3).

3.10 Treatment of high strength steel. When specified, steel parts having an ultimate tensile strength of 200,000 psi (1379 MPa) or above shall be baked at 375 ± 25 F (191 ± 14 C) for three hours or more or given an equivalent embrittlement relief treatment after application of the oxide coating. Coated springs or other parts subject to flexure shall not be flexed prior to the baking operation. When specified by the procuring activity, high strength steel parts shall be tested in accordance with 4.4.4 for embrittlement relief. If an embrittlement relief bake is required, it shall follow the chromic acid rinse. The embrittlement relief precedes the supplmentary preservative treatment.

3.11 Supplementary preservative. Materials for supplementary preservative treatments and methods of application shall be in accordance with the applicable requirements of the end item specification, or as otherwise specified. Unless otherwise specified, the supplementary preservative treatment shall be applied to the clean and dry parts immediately following the hot dilute chromic acid dip.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the supplier 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 the specification where such inspections are deemed necessary to assure that supplies and services conform to prescribed requirements.

4.2 Lot. A lot shall consist of coated parts of the same class, same basis metal, and approximately the same size and shape and coated under similar conditions. A maximum of 8 hours continuous production shall constitute a lot.

4.3 Sampling. Single sample plan for normal inspection of the classification of defects shall be in accordance with MIL-STD-105.

4.3.1 Sampling for nondestructive tests (visual inspection, coverage, color, smut, and workmanship). Samples shall be selected at random from each inspection lot in accordance with MIL-STD-105, inspection level I, and acceptable quality level (AQL) equal 1.0 percent defective.

4.3.2 Sampling for destructive tests (oxalic acid spot test, salt spray test, and embrittlement relief test). Samples shall be selected at random from each inspection lot in accordance with MIL-STD-105, inspection level S-1 and acceptable quality level (AQL) equal to 1.0 percent defective.

4.4 Test procedures.

4.4.1 Smut test. Test shall be made prior to application of corrosion preventive compound or after vapor degreasing. Each black oxide coated piece shall be inspected visually under strong light to assure a satisfactory appearance. Each sample shall also be wiped with a clean white cloth for indications of smut (see 3.7). A slight amount of smut which is inherent in the process is acceptable for all classes of coatings and shall not be cause for rejection.

4.4.2 Oxalic acid spot test (classes 1 and 3). The black oxide coated pieces of classes 1 and 3 only, prior to the application of a preservative, shall be handled with clean cotton gloves or the equivalent. Each sample shall have deposited, on one flat spot of the black oxide coated surface, three drops (0.2 ml) of a five percent solution of oxalic acid. The reaction shall be observed after 30 seconds and up to eight minutes. After eight minutes the panel shall be rinsed and compared to figures 1, 2, and 3. A light grey center with a lighter border color (figure 1) indicates a poor quality coating. A grey-black center with a light border (figure 2) indicates a borderline quality coating. The coating shall conform to the good quality coating of figure 3 to be acceptable. A black or dark brown center with a light border (figure 3) indicates a good quality coating. A good quality coating may show a light border, indicating exposure of metal around the drops. Parts shall therefore be judged only on the color and exposure of the metal under the drops.

4.4.3 Resistance to salt spray (class 4). The coated pieces of class 4 (AISI type 300 series corrosion resistant steel) shall be subjected to a 5 percent salt spray (fog) test in accordance with ASTM B 117. Exposure time for the black coatings, prior to the application of a preservative, or after vapor degreasing, shall comply with the requirements of 3.9.

4.4.4 Embrittlement relief. To test for embrittlement, the use of notched tensile samples may be used when specified. Samples selected in accordance with 4.3.2 for determining compliance with 3.10, shall be subjected to a sustained tensile test as specified by the procuring activity, or using loads applicable to the parts as contained herein. The articles or parts shall be held under the load for at least 200 hours unless otherwise specified, and then examined for cracks. The lot shall be rejected if any coated part develops cracks or fails by fracture.

4.4.4.1 Fasteners. Parts such as steel fasteners, threaded or not threaded, which are used for mechanical joining of metal shall be subjected to a sustained tensile loading not less than 75 percent of the material specification minimum ultimate tensile strength.

4.4.4.2 Spring pins, lock rings, etc. Parts such as spring pins, lock rings, etc., which are installed in holes as rods shall be similarly assembled using the applicable parts specification as drawing tolerances which impose the maximum sustained tensile stress on the coated parts.

4.4.4.3 Other parts. Other parts, that will be subjected to a sustained static tensile load in excess of 25 percent of the material specification minimum tensile yield strength in service use, shall be subjected to a sustained tensile load equal to 75 percent of the material specification minimum tensile yield strength.

5. PACKAGING

5.1 Preparation for delivery is not applicable to this specification.

6. NOTES

6.1 Intended use. Black oxide coatings are particularly suited for moving parts that cannot tolerate the dimensional build-up of a more corrosion-resistant finish. They are not recommended on parts going into long-term storage. Sometimes, long term storage is required and a protective preservative fluid is recommended or a desiccated package is utilized. The coatings present a pleasing black appearance frequently employed for decorative purposes or decrease in light reflection. A supplementary water displacing preservative coating such as MIL-C-16173, grade 3 or VV-L-800 or comparable material which will provide equal or superior corrosion protection may be specified.

CAUTION: High strength steel (Rockwell C40 or greater hardness) may be subjected to "caustic embrittlement" that could lead to spontaneous cracking if under internal or applied stress during the blackening treatment.

6.1.1 Organic finishes. Black oxide coatings are not primarily used as pretreatment coatings for paint and lacquer. A phosphate base coating (TT-C-490, type I, or DOD-P-16232, type Z, class 3) gives better corrosion resistance and is preferred.

6.2 Ordering data. Purchasers should exercise any desired options offered herein, and procurement documents should specify the following:

a. Title, number, and date of this specification.

b. Class of coating (see 1.2).

c. Embrittlement relief treatment and test, if applicable (see 3.10 and 4.4.4).

d. Supplementary preservative treatment if required (see 3.11 and 6.1).

6.3 Miscellaneous notes.

6.3.1 Dimensional change. Black oxide coatings on iron and steel should produce no appreciable dimensional change of the treated piece. The dimensions shown on the drawings are, therefore, the dimensions after the application of the coatings.

6.3.2 Processing. Contractors may employ one of a number of trade-name black-finishing oxidizing materials or prepared chemical mixtures to apply the black oxide coating. The processing details should conform to MIL-HDBK-205, or as recommended by the raw material supplier. Table I provides an outline of the various processes.

TABLE I. Materials and processing procedures.

Class	Applicability to ferrous metals	Process and possible chemicals	Approximate processing temperature	Approximate immersion time
1	Carbon steels, low alloy steels, wrought irons, cast and malleable irons	Alkaline oxidizing, NaOH, $NaNO_3$, water	1 or 2 tanks boiling at 285 - 305 F (141 - 152 C)	5 to 60 min
3	For corrosion resistant steel alloys which are tempered at 900 F (482 C) or higher	Fuzed salt oxidizing $Na_2Cr_2O_7$ and/or $K_2Cr_2O_7$	Molten bath 750 - 850 F (399 - 454 C)	30 min
4	For 300 series corrosion resistant steel alloys, only	Alkaline oxidizing, proprietary compounds plus water.	250 - 265 F (121 - 130 C)	15 to 30 min

6.3.3 Cast and malleable irons. Cast and malleable irons may be more effectively treated in class 4 proprietary baths. They have not been included in table I because of the class 4 salt spray requirement.

6.3.4 Class 4 coatings. Corrosion resisting steels of minimum composition 17 Cr - 7 Ni can be effectively blackened by this process.

6.3.5 Rinsing. In order to obtain effective removal of blackening solution and ensure thorough rinsing, a combination of spray rinses with tank rinses or a properly operated double counterflow rinse operation may be advantageous. Use of such a system may help reduce the amount of water required to obtain a desired rinsing criterion and facilitate meeting the EPA standard.

Custodians:
Army - MR
Navy - OS
Air Force - 11

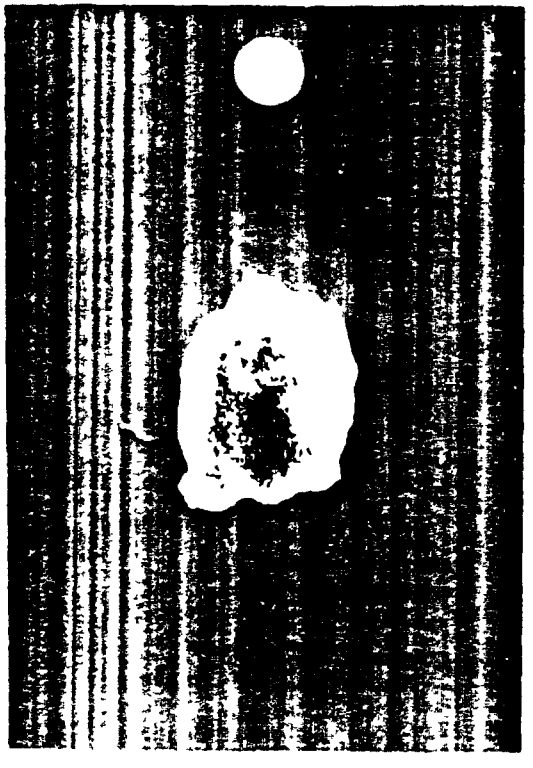
Review activities:
Army - AR, MI, EA
Navy - AS
Air Force - 99

User activity:
Army - ME, AV
Navy - SH
Air Force - 68

Preparing activity
Army - MR

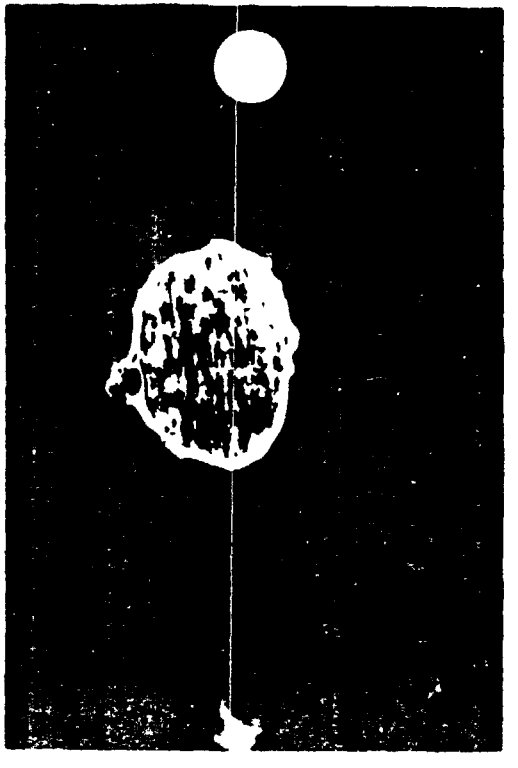
Project No. MFFP-0147

OXALIC ACID SPOT TESTS ON BLACK OXIDE COATINGS



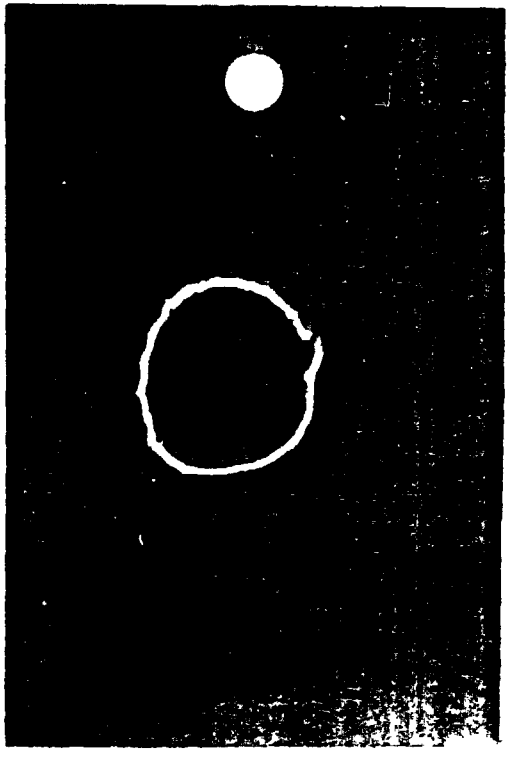
A POOR QUALITY COATING

Figure 1



A BORDERLINE QUALITY COATING

Figure 2



A GOOD QUALITY COATING

Figure 3

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4 TYPE OF ORGANIZATION *(Mark one)*

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- ☐ USER
- ☐ MANUFACTURER
- ☐ OTHER *(Specify)* _____

b ADDRESS *(Street, City, State, ZIP Code)*

5 PROBLEM AREAS

a. Paragraph Number and Wording

b Recommended Wording

c Reason/Rationale for Recommendation

6 REMARKS

7a NAME OF SUBMITTER *(Last, First, MI)* – Optional

b WORK TELEPHONE NUMBER *(Include Area Code)* – Optional

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8 DATE OF SUBMISSION *(YYMMDD)*

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