NOT MEASUREMENT SENSITIVE

MIL-DTL-13924D
18 March 1999
SUPERSEDING
MIL-C-13924C
9 June l980

DETAIL 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 should be of the following classes as specified (see 6.2 and 6.3.2).

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

Class 2 Alkaline chromate oxidizing process (for use on certain corrosion resistant steel alloys which are tempered at less than 900°F (482°C)).

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 other corrosion resistant steel alloys).

Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Director, U.S. Army Research Laboratory, Weapons and Materials Research Directorate, ATTN: AMSRL-WM-M, Aberdeen Proving Ground, MD 21005-5069 by using the Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

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 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 documents cited in sections 3 and 4 of this specification, whether or not they are listed.

2.2 Government documents.

2.2.1 Specifications, standards, and handbooks. The following specifications, standards, and handbooks form a part of this document to the extent specified herein. Unless otherwise specified, the issues of these documents are those listed in the issue of the Department of Defense Index of Specifications and Standards(DoDISS) and supplement thereto, cited in the solicitation (see 6.2).

SPECIFICATIONS

DEPARTMENT OF DEFENSE

MIL-C-53072 Chemical Agent Resistant Coating (CARC) System Application Procedures And Quality Control Inspection

(Unless otherwise indicated, copies of the above specifications, standards, and handbooks are available from the Defense Automated Printing Service (DAPS), Building 4D, 700 Robbins Avenue, Philadelphia, PA 19111-5094).

2.3 Non-Government publications. The following documents form a part of this document to the extent specified herein. Unless otherwise specified, the issues of the documents which are DoD adopted are those listed in the issue of the DoDISS cited in the solicitation. Unless otherwise specified, the issues of documents not listed in the DoDISS are the issues of the documents cited in the solicitation (see 6.2).

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)

ASTM B117 Operating Salt Spray (Fog) Apparatus (DoD adopted)

ASTM F519 Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals

(Application for copies should be addressed to the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.)

SOCIETY OF AUTOMOTIVE ENGINEERS, INC. (SAE)

AMS 2759/9 Hydrogen Embrittlement Relief (Baking) Of Steel Parts

(Application for copies should be addressed to the Society Of Automotive Engineers, Inc., 400 Commonwealth Drive, Warrendale, PA 15096.)

2.4 Order of precedence. 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 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. The cleaned surfaces shall be free of rust, scale, grease, oil, paint, or other foreign matter, and shall pass the water break test described in MIL-C-53072. Cleaning materials and methods shall be at the option of the contractor. The cleaning process shall be performed without measurable abrasion or erosion.

3.2.1 Stress relief. Unless otherwise specified for a particular end item specification or drawing, after forming and hardening, and prior to cleaning and coating, objectionable residual stress in ferrous alloy parts having a hardness greater than 40 HRC shall be relieved by suitable heat treatment. The temperature shall be such that maximum relief is given without hardness being reduced to less than the specified minimum. Stress relief is not necessary where it has been demonstrated that coating has no harmful effect on the coated part.

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.

3.4 Alkaline oxidizing solutions (classes 1 and 2). Classes 1 and 2 oxide coatings shall be formed from a boiling alkaline oxidizing or alkaline chromate oxidizing solution, respectively.

3.4.1 Rinsing. All classes of black oxide coated pieces shall be rinsed in cold water.

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 l50 to l90°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, l90°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. Class 1, 2, 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 Oxalic acid spot test (class 1, 2, and 3). The black oxide coatings of classes 1, 2, 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 preservative, shall show no signs of corrosion after 96 hours of exposure in the salt spray test (see 4.4.3).

3.10 Hydrogen embrittlement relief treatment. Steel parts that are surface or through hardened at 40 HRC and above shall be given a hydrogen embrittlement relief treatment after application of the oxide coating. Coated springs or other parts subject to flexure shall not be flexed prior to the embrittlement relief treatment. If an embrittlement relief treatment is required, it shall follow the chromic acid rinse. The embrittlement relief treatment precedes the supplementary 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 after the final stage of processing.

3.12 Workmanship. The surface of the coated part shall be uniform in appearance and free of visible coating defects, such as blisters, pits, roughness, nodules, burning, cracks, or uncoated areas, and other defects that will affect the function of the coating. The coated parts shall be clean and free of damage.

4. VERIFICATION

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the contractor is responsible for the performance of all inspection requirements (examinations and tests) as specified herein. Except as otherwise specified in the contract or purchase order, the contractor may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by 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 ensure supplies and services conform to prescribed requirements.

4.1.1 Classification. All the tests required for the testing are classified as quality conformance tests, for which necessary sampling techniques and the methods of testing are specified in this section.

4.2 Sampling.

4.2.1 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.

4.2.2 Selection. The number of random samples selected for nondestructive tests (visual inspection, coverage, color, smut, and workmanship), and destructive tests (oxalic acid spot test, salt spray test, and embrittlement relief test) from each lot of coated parts shall be defined by the procuring activity (see 6.2).

4.3 Acceptance and rejection. The selected coated parts shall meet the requirements in this specification for the represented lot to be acceptable. Failure of any test samples to meet the requirements in this specification shall constitute rejection of the entire lot which they represent. Unless otherwise specified (see 6.2), the tests shall be conducted and the test results accepted prior to shipment of the lot of coated parts represented by the test samples.

4.3.1 Surface attack. Parts shall be examined for pitted surfaces or intergranular attack by viewing them at magnifications up to 10x.

4.4 Test procedures.

4.4.1 Smut test. The 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 (class 1, 2, and 3). The black oxide coated pieces of classes 1, 2, 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 (0.00676 oz. (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 gray center with a lighter border color (figure 1) indicates a poor quality coating. A gray-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 B117. 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 Hydrogen embrittlement relief treatment. When specified (see 6.2), ferrous parts shall be baked in accordance with AMS 2759/9, table 1.

4.4.4.1 Hydrogen embrittlement relief test. Samples selected in accordance with 4.2.2 to determine the adequacy of the hydrogen embrittlement relief treatment, shall be tested in accordance with ASTM F519. When specified (see 6.2), the standard notched round bar specimen under load control described in annex A1, which is a part of ASTM F519, shall be used. The lot shall be rejected if any coated specimen develops any crack or fails by fracture as a result of the test.

5. PACKAGING

5.1 Packaging. Packaging requirements are not applicable to this specification.

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 black oxide coatings covered by this specification are military unique. Black oxide coatings are used on munition cases and gun barrels. These 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-PRF-16173, grade 3 or comparable material which will provide equal or superior corrosion protection may be specified.

CAUTION: High strength steel (40 HRC 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.

6.2 Acquisition requirements. Acquisition documents should specify the following:

(a) Title, number, and date of this specification.
(b) Class of coating (see 1.2).
(c) Issue of DoDISS to be cited in the solicitation, and if required, the specific issue of individual documents referenced (see 2.2.1 and 2.3).
(d) Number of samples to be inspected from the lot of coated parts (see 4.2.2).
(e) Acceptance requirements prior to shipment of the coated parts, if different (see 4.3).
(f) Bake ferrous parts in accordance with AMS 2759/9, table 1 (see 4.4.4).
(g) Use the standard notched round bar specimen under load control described in annex A1, which is a part of ASTM F519 (see 4.4.4.1).

6.3 Miscellaneous notes.

6.3.l 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, “Phosphatizing and Black Oxide Coating of Ferrous Metals”, or as recommended by the material supplier. Class 2 is used to process the 4XX series corrosion resisting steels, class 3 is used for 3XX and 4XX series, and class 4 is used to process those 300 series corrosion resisting steels which can meet the special salt spray test criteria and for those 4XX series corrosion resisting steels which do not have any special salt spray test criteria. Table I provides an outline of the various processes.

6.3.3 Cast and malleable irons, and certain 400 series corrosion resistant steels. Cast and malleable irons and 400 series corrosion resistant steels of the martensitic type can also be effectively treated in Class 4 proprietary baths, but will not meet the salt spray requirement of austenitic 300 series corrosion resistant steels.

6.3.4 Class 4 coatings. Corrosion resisting steels of minimum composition l7Cr-7Ni 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.

6.3.6 Ozone depleting chemicals. Classes I and II ozone depleting chemicals should be avoided when cleaning the basis metal.

6.3.7 Hazardous materials. The DoD has put together a list of hazardous or environmentally damaging substances in a document called the SD-14. These chemicals should be avoided whenever another finish can be substituted for the finish specified herein.

6.4 Subject term (key word) listing.

Chromic acid dip
Chromium compounds
Embrittlement relief
Oxalic acid spot test
Preservative
Salt spray
Smut test

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

CONCLUDING MATERIAL

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

Review activities:
Army - MI, PT
Navy - AS, EC, SH
Air Force - 13, 19
DLA - DH(DCMC-OF, DLSC-LEQ)

Preparing activity:
Army - MR

(Project MFFP-0664)

TABLE I. Materials and processing procedures.

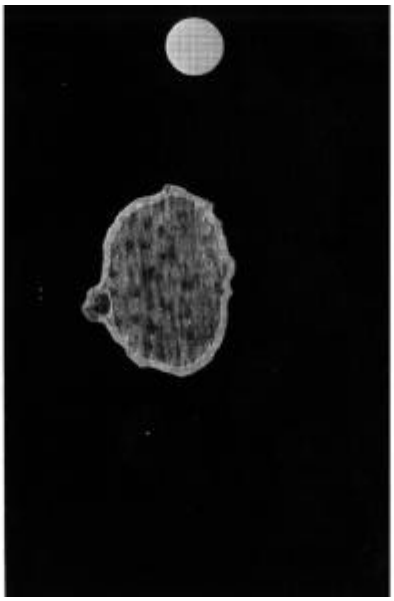
Class	Applicability to ferrous metals	Process and possible chemicals	Approximate processing temperature	Approximate immersion time
1	Carbon steels, low alloy steels, wrought irons, cast and malleable irons	Alkaline oxidizing, NaOH, $NaNO_3$, water	1 or 2 tanks boiling at 285 - 305°F (141 - 152°C)	5 to 60 min.
2	Certain corrosion resistant steel alloys which are tempered at less than 482°C	Alkaline chromate NaOH, $NaNO_3$, $Na_2Cr_2O_7$ 1/, Water	250°F ± 10°F (121°C ± 5°C)	30 to 45 min.
3	For corrosion resistant steel alloys which are tempered at 900°F (482°C) or higher	Fused salt oxidizing $Na_2Cr_2O_7$ 1/ and/or $K_2Cr_2O_7$ 1/	Molten bath 750 - 850°F (399 - 454°C)	30 min.
4	For corrosion resistant steel alloys	Alkaline oxidizing, proprietary compounds plus water	250 - 265°F (121 - 130°C)	15 to 30 min.

1/ Chromium compounds.

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.

STANDARDIZATION DOCUMENT IMPROVEMENT PROPOSAL

INSTRUCTIONS

1. The preparing activity must complete blocks 1, 2, 3, and 8. In block 1, both the document number and revision letter should be given.

2. The submitter of this form must complete blocks 4, 5, 6, and 7.

3. The preparing activity must provide a reply within 30 days from receipt of the form.

NOTE: This form may not be used to request copies of documents, nor to request waivers, or clarification of requirements on current contracts. Comments submitted on this form do not constitute or imply authorization to waive any portion of the referenced document(s) or to amend contractual requirements.

I RECOMMEND A CHANGE:	**1. DOCUMENT NUMBER** MIL-DTL-13924D	**2. DOCUMENT DATE (YYMMDD)** 990318

DOCUMENT TITLE **COATING, OXIDE, BLACK, FOR FERROUS METALS**

4. NATURE OF CHANGE *(Identify paragraph number and include proposed rewrite, if possible. Attach extra sheets as needed.)*

5. REASON FOR RECOMMENDATION

6. SUBMITTER

a. NAME *(Last, First, Middle Initial)*	b. ORGANIZATION	
c. ADDRESS *(Include Zip Code)*	d. TELEPHONE (Include Area Code) (1) Commercial (2) AUTOVON *(if applicable)*	**7. DATE SUBMITTED** (YYMMDD)

8. PREPARING ACTIVITY

a. NAME US ARM RESEARCH LABORATORY	b. TELEPHONE *Include Area Code)* (1) Commercial 410-306-0725 (2) AUTOVON 458-0725
c. ADDRESS *(Include Zip Code)Commander* WEAPONS AND MATERIALS RESEARCH DIRECTORATE ATTN; AMSRL-WM-M ABERDEEN PROVING GROUND, MD 21005-5069	**IF YOU DO NOT RECEIVE A REPLY WITHIN 45 DAYS, CONTACT:** DEFENSE QUALITY AND STANDARDIZATION OFFICE 5203 Leesburg Pike, Suite 1403, Falls Church, VA 22401-3466 Telephone (703) 756-2340 AUTOVON 289-2340