MIL-P-15169B(SHIPS)
24 December 1963
SUPERSEDING
MIL-P-15169A(SHIPS)
21 March 1960
(See 6.2)

MILITARY SPECIFICATION

PIGMENT, CUPROUS OXIDE

1. SCOPE

1.1 This specification covers cuprous oxide pigment used as an ingredient in the manufacture of paint and entirely suitable for use as the toxic in the manufacture of antifouling paints.

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 the specification to the extent specified herein.

SPECIFICATIONS

FEDERAL
RR-S-366 - Sieves, Standard for Testing Purposes.

STANDARDS

FEDERAL
FED-STD-141 - Paint, Varnish, Lacquer, and Related Materials Methods of Inspection, Sampling, and Testing.

(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.)

3. REQUIREMENTS

3.1 Material. - Cuprous oxide shall be furnished in the form of dry pigment, free from adulterants.

3.2 Chemical composition. - Cuprous oxide shall conform to the chemical composition specified in table I.

Table I - Chemical composition.

	Minimum	Maximum	Applicable Test Paragraph
	Percent	Percent	
Cuprous-oxide (Cu_2O) (when free copper is present)	95.0	----	4.3.10
Cuprous-oxide (Cu_2O) plus free copper	97.0	----	4.3.9, 4.3.10
Total copper (Cu)	86.0	----	4.3.2
Total reducing power as Cu_2O	97.0	----	4.3.8
Chlorides as Cl	----	0.4	4.3.4.2
Sulphates as SO_4	----	.1	4.3.4.3
Acetone soluble matter	----	.5	4.3.5
Nitric acid insoluble	----	.3	4.3.1
Residue on No. 325 mesh sieve (Spec. RR-S-366)	----	.5	4.3.6
Metals other than copper	----	.5	4.3.3
Water	----	.5	4.3.7
Stability: loss of total reducing power	----	2.0	4.3.12

FSC 8010

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 supplies and services conform to prescribed requirements.

4.2 Sampling, inspection and testing. - Sampling, inspection and testing shall be in accordance with method 1031.1 of Standard FED-STD-141. All tests shall be run for each lot.

4.3 Test procedures. -

4.3.1 Insoluble in nitric acid. - Weigh accurately 1.0 gram (gm.) of the sample, transfer to a 250 millilter (ml.) beaker, add 10 ml. of nitric acid (sp. gr. 1.42) and boil for several minutes. Cool and dilute with 100 ml. of water. Allow residue to settle and filter off insoluble matter through a weighed Gooch crucible with an asbestos mat or a coarse porosity fritted glass Gooch crucible. Wash with hot water and hot 10 percent nitric acid and finally with hot water to remove all copper salts. Dry crucible for 1 hour at 105° centigrade (°C.), cool, and weigh. Report as insoluble in nitric acid and save filtrate for total copper determination (see 4.3.2).

4.3.2 Total copper. - To filtrate from acid insoluble determination in 300 ml. electrolytic beaker, add 10 ml. perchloric acid and fume for 5 minutes, cool, dilute to volume of about 150 ml., add 1 ml. of concentrated nitric acid, 1 gm. ammonium sulfate and electroplate copper on platinum electrode at about 2 amperes current for 2 hours. Dilute with water and if the electrolysis is complete, remove electrode, wash with water and acetone, weight, and report as total copper. Save the electrolyte for the determination of metals other than copper. (see 4.3.3)

4.3.3 Metals other than copper. - Filter the electrolyte from the determination of copper (see 4.3.2), add 5 ml. of concentrated sulfuric acid (sp. gr. 1.84) and evaporate just to dryness to remove all perchloric and nitric acids. Add approximately 150 ml. of water, neutralize with ammonium hydroxide (sp. gr. 0.90) and add 5 ml. ammonium hydroxide (sp. gr. 0.90) in excess. Finally add 10 gm. of chemically pure ammonium chloride. Boil the solution gently for several minutes and allow the precipitate to settle. Filter through No. 589 "S and S" Blue Ribbon paper or equal and wash the precipitate with 50 ml. of hot 2 percent ammonium chloride solution. Save the filtrater for the zinc determination. Dissolve the precipitate from the filter paper with hot (1:1) hydrochloric acid and determine the iron by the usual procedure of reduction with stannous chloride solution followed by addition of mercuric chloride and titration with ceric sulfate. Calculate as percent metallic iron (Fe). Evaporate the filtrate to 15-20 ml. If the solution is colored, the presence of nickel and/or cobalt may be indicated and shall be determined by any standard procedure and reported as percent cobalt or nickel. Neutralize the solution with 1:2 sulfuric acid and add 15 ml. in excess. Dilute to 300 ml. with water. Add 10 drops of potassium ferricyanide solution (see 4.4.7), and 5 drops of diphenylamine indicator (see 4.4.9). Heat to 75° C. and titrate with standard potassium ferrocyanide solution (see 4.4.8). A color change from blue to greenish yellow occurs at the end point. Calculate as percent zinc (Zn). Add the percents of metals found and report as percent metals other than copper.

4.3.4 Determination of chlorides and sulfates

4.3.4.1 Preparation. - Weight accurately approximately 10 gm. of the sample, add an excess of nitric acid, heat gently until sample is decomposed. Dilute with distilled water until the volume is approximately 150 ml. Add an excess of a solution of sodium carbonate (Na_2CO_3) that is free of both Cl and SO_4, and bring to a boil. Transfer to a 500-ml. volumetric flask and fill to the mark with distilled water. Let settle. Draw off two separate portions of 50 ml. each of the clear solution. Make each slightly acid with nitric acid. Use one for the determination of chlorides and one for the sulfates as required below.

4.3.4.2 Chlorides. - To one of the solutions prepared as specified in 4.3.4.1, add a few drops of a solution of silver nitrate ($AgNO_3$). If no precipitate forms, report no chlorides present. If a precipitate forms, add slowly an excess of silver nitrate solution, heat to boiling after the precipitate has settled, filter through a Gooch crucible, wash with cold water, dry at 130°C., cool, weigh, and compute as percentage of Cl (weight of AgCl x 0.247 = Cl).

4.3.4.3 Sulfates. - To the second solution prepared as specified in 4.3.4.1, add a few drops of a 10-percent solution of barium chloride ($BaCl_2$). If no precipitate is formed, report no sulfate present. If a precipitate forms, dilute to approximately 200 ml., add approximately 1 ml. of 1:1 hydrochloric acid. Heat to boiling and add slowly an excess of barium chloride ($BaCl_2$) solution. Let settle, filter through a Gooch crucible, wash, dry, ignite at a dull red heat, cool in a desiccator and weigh ($BaSO_4$ x 0.412 = SO_4).

4.3.5 Matter soluble in acetone. - Weigh accurately 5 gm. of the well mixed sample and transfer to a 250-ml. glass stoppered Erlenmeyer flask. Add 100 ml. of acetone and shake vigorously for 15 minutes. Allow to settle and filter through a close double filter paper such as "S and S" Blue Ribbon into a 250-ml. Griffin beaker. Wash flask and paper well with acetone to remove all acetone soluble matter. Evaporate off acetone on water bath to low volume and transfer to 15 by 55-mm. weighed aluminum moisture dish. Wash out beaker with small amount of acetone. Finally evaporate off all acetone and heat for 30 minutes in oven at 105°C. Residue is acetone soluble matter.

4.3.6 Coarse particles. - Determine the percentage of coarse particles on a 25-gm. sample as specified in method 4101 of FED-STD-141, using a No. 325 mesh sieve conforming to RR-S-366.

4.3.7 Water. - Determine the percentage of moisture on a 50-gm. sample using the distillation method specified in method 4081 of FED-STD-141 and employing xylol as a solvent. Bring the extract (water) to a temperature of 25°C., note volume in ml. and convert volume to weight by multiplying by 0.997 to obtain the weight of the water extracted. Convert to percent.

4.3.8 Total reducing power as cuprous oxide. - Weigh accurately 0.2 gm. of well mixed sample[1/] and place in a 250-ml. vented glass stoppered Erlenmeyer flask previously filled with CO_2 gas. (Dry ice is preferable) Add a few small glass beads and 10 ml. of ferric chloride solution (see 4.4.1). Heat gently for 15 minutes, stirring occasionally and maintaining a CO_2 atmosphere at all times. After the sample has been dissolved, cool, add 50-ml. distilled water and titrate at once with 0.1 N ceric sulfate solution (see 4.4.2) until approximately near the end point. Add two drops of orthophenanthroline (ferrous complex) indicator (see 4.4.6), and complete the titration. A sharp, distinct color change from orange to pale green occurs at the end point. Back titrate with 0.03 N ferrous ammonium sulfate (see 4.4.3) to the orange color. Subtract the ferrous ammonium sulfate equivalent from the total titration and calculate as total reducing power as cuprous oxide.

4.3.9 Metallic copper. - Add approximately 20 ml. of 4 mm. diameter glass beads to a 250 ml. extraction flask. Weigh accurately a sample of suitable size (0.15 to 1 gm.) depending on the metallic copper content on a tared, glazed paper approximately 1/2 square inch in size and transfer the sample and paper to the flask. Add 25 ml. of denatured alcohol (see 4.4.4) and swirl vigorously for approximately 1 minute to remove any surface coating and break up lumps. (Then keep under an atmosphere of CO_2 during the entire remaining operations). Add slowly while swirling the flask, 100 ml. of the extraction solution (see 4.4.5). After the addition of the extraction solution, swirl the flask vigorously for 5 minutes, adding lumps of dry ice continuously during this time to lower the temperature of the solution to approximately minus 10°C. (The solution must be kept very cold in order to get correct and reproducible results.) Rapidly filter the solution through the prepared Gooch crucible[2/] using suction. (If particles are noticed going through the pad, the determination must be discarded and a heavier pad used). Continue the addition of dry ice to the flask and filter paper during the filtration to keep the solution cold. Wash the flask and paper with 150 to 200 ml. of denatured alcohol, continuing to use suction. Transfer the entire residue, filter paper and beads to the original extraction flask and dissolve the residue in 25 ml. of the ferric chloride - hydrochloric acid solution (see 4.4.1) keeping an atmosphere of CO_2 above the sample by addition of dry ice. Heat on a steam bath to dissolve the copper. Add 50 ml. of distilled water and 3 drops of orthophenanthroline indicator (see

1/ The use of a 0.4-ml. capacity micro beaker for weighing the sample, is advised. The beaker is weighed first and the sample introduced into the beaker, the correct weight obtained and the entire beaker and its contents dropped into the flask. This eliminates errors in weighing caused by brushing the sample from glass balance pans.

2/ In the preparation of the filter pulp pad for the Gooch crucible used in the filtration, care must be taken to see that the pad is sufficiently thick and compressed to prevent any very finely divided particles from going through the filter pad. A compressed filter pad approximately 3/8 inch in thickness will usually prevent the finely divided particles from going through the pad. The pad is best prepared in layers, using suction and compressing each layer. The prepared Gooch crucible is washed with denatured alcohol prior to use.

4.4.6). Titrate with the standard ceric sulfate solution (see 4.4.2) until the color changes from orange to pale green. Calculate the metallic copper content as follows:

$$\text{Percent of copper} = \frac{\text{gm. cu/ml. of ceric sulfate solution X ml. ceric sulfate X 100}}{\text{weight of sample}}$$

4.3.10 Cuprous oxide.- Multiply the percent metallic copper by 2.252 and subtract this percentage from percent total reducing power as cuprous oxide. The difference is the percent of cuprous oxide.

4.3.11 Cupric oxide.- Calculate the percentage of cupric oxide from the values determined for metallic copper (see 4.3.9), cuprous oxide (see 4.3.10) and total copper (see 4.3.2) as follows:

$c - (a + b) = d$ is percent copper as Cu
$d \times 1.252 =$ percent CuO

Where:
a = Percent $Cu_2O \times 0.888$ = percent copper from Cu_2O.
b = Percent metallic copper determined as specified in 4.3.9
c = Percent total copper determined as specified in 4.3.2

4.3.12 Stability test.-

4.3.12.1 Spread approximately 100 gm. of the sample on a watch glass and heat in an oven at a temperature of 100°F and approximately 95 percent relative humidity for a period of 72 hours. Remove from the oven. Note any change in color of the sample. Determine total reducing power, using the method described in 4.3.8.

4.3.12.2 Determine the percentage of moisture on a 50 gm. sample after treatment for stability, using the distillation method described in method 4081 of Standard FED-STD-141 and employing xylene as a solvent. Bring the extract (water) to a temperature of 25°C., note volume in ml. and convert volume to weight by multiplying by 0.997 to obtain the weight of the water extracted. Convert to percent.

4.3.12.3 Calculate the percent of decrease in total reducing power after stability treatment as follows: Compute the percent of total reducing power after stability based on the dry sample from the values obtained by the method specified in 4.3.8. Subtract this value from the percent total reducing power of the original (see 4.3.8), multiply the difference by 100 and divide by the total reducing power of the original sample. Report as percent decrease in total power after stability treatment.

4.4 Reagents.-

4.4.1 Ferric chloride solution.- Add 75 gm. of $FeCl_3 \cdot 6H_2O$ and 150 ml. of HCl. (sp.gr. 1.19) to 400 ml. of CO_2 saturated distilled water. Stir to complete solution. Keep solution saturated with CO_2.

4.4.2 Ceric sulphate solution 0.1 N.- Weigh 33.3 gm. of anhydrous ceric sulphate into a 600 ml. beaker and add 26 ml. of concentrated H_2SO_4. Dilute with 25 ml. of water. Boil for 10 minutes, stirring constantly. Stir in small additions of water, heating until all the sample is dissolved. Transfer to a liter volumetric flask and dilute to the mark. This solution must be aged several weeks to allow all suspended matter to precipitate. Filter. Standardize against electrolytic iron or ferrous ammonium sulphate.

4.4.3 Ferrous ammonium sulfate 0.03 N.- Dissolve 12 gm. of Mohr's salt in 200 to 300 ml. of water and add 40 ml. of concentrated sulfuric acid, stirring constantly. Dilute to 1 liter in a volumetric flask. A few pieces of mossy aluminum may be added to stabilize the solution. The solution should be restandardized frequently with 0.1 N ceric sulfate solution.

4.4.4 Denatured alcohol, Formula No. 2B.- To 995 ml. of 95 percent ethyl alcohol add 5 ml. of benzene.

4.4.5 Extraction solution. - Add 40 ml. of concentrated chemically pure hydrochloric acid (sp. gr. 1.19) to 1 liter of denatured alcohol. Mix thoroughly. Add 40 gm. of fresh, chemically pure stannous chloride ($SNCl_2 \cdot 2H_2O$) and stir until completely dissolved. Solution remains more stable if stored under refrigeration (40-50°F).

4.4.6 Orthophenanthroline indicator. - Orthophenanthroline ferrous complex (ferroin)[3/] shall be used as indicator.

4.4.7 Potassium ferricyanide solution - 5 percent. - Dissolve 5 gm. of pure reagent grade potassium ferricyanide ($K_3Fe(CN)_6$) in 95 ml. of distilled water. Keep lightly stoppered in a dark bottle.

4.4.8 Standard potassium ferrocyanide solution. - Dissolve 5.0 gm. of pure reagent grade potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) in distilled water and dilute to 1 liter and standardize with analyzed chemically pure zinc. Standardize the solution prior to use.

4.4.9 Diphenylamine indicator solution. - Dissolve 1 gm. of diphenylamine in 100 ml. of concentrated sulfuric acid (sp. gr. 1.84).

4.4.10 Acetone. - Chemically pure reagent.

4.4.11 Rejection. - Use of the lot shall not be permitted until a favorable report is received from the testing laboratory. Non-compliance with any one of the requirements shall be cause for rejection of the lot.

5. PREPARATION FOR DELIVERY

5.1 Not applicable

6. NOTES

6.1 This specification covers an ingredient for use in specifications for paints and related materials and as such is not intended for use for direct procurement by the Government. In the event a purchase is made, suitable preparation for delivery requirements should be made a part of the contract. The quality assurance provisions are provided for use in connection with inspection of this cuprous oxide pigment when used as an ingredient in paints purchased for the Government.

6.2 CHANGES FROM PREVIOUS ISSUE. THE EXTENT OF CHANGES (DELETIONS, ADDITIONS, ETC.) PRECLUDE THE ANNOTATION OF THE INDIVIDUAL CHANGES FROM PREVIOUS ISSUE OF THIS DOCUMENT.

[3/] Manufactured by G. Fredrick Smith Chemical Company, Columbus, Ohio

Preparing activity:
Navy - Ships
(Project 8010-N049Sh)

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STANDARDIZATION DOCUMENT IMPROVEMENT PROPOSAL

(See Instructions – Reverse Side)

1. DOCUMENT NUMBER	2. DOCUMENT TITLE
Notice 2 MIL-P-15169B(SHIPS)	PIGMENT, CUPROUS OXIDE

3a. NAME OF SUBMITTING ORGANIZATION	4. TYPE OF ORGANIZATION *(Mark one)*
	☐ VENDOR
b. ADDRESS *(Street, City, State, ZIP Code)*	☐ USER
	☐ MANUFACTURER
	☐ OTHER *(Specify)*: _____

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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