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BUREAU OF STANDARDS

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RECOMMENDED SPECIFICATION FOR OCHER, DRY AND PASTE

PREPARED AND RECOMMENDED BY THE UNITED STATES INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATIONS STANDARDIZATION, MARCH 22, 1920. P. H. WALKER, BUREAU OF STANDARDS, CHAIRMAN; H. E. SMITH, UNITED STATES RAILROAD ADMINISTRATION, SECRETARY

[This committee was appointed at the suggestion of the Secretary of Commerce, and consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Railroad Administration, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The committee submitted a preliminary draft of the specification to a large number of paint manufacturers and gave careful consideration to the replies received.]

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1. GENERAL

Ocher may be required in the form of dry pigment or paste ground in linseed oil; it shall be prepared in accordance with the most improved methods. Grinding in oil shall be thorough and the vehicle shall be pure raw linseed oil.

The material shall be bought by net weight.

(a) DRY PIGMENT.—The pigment shall be a hydrated oxide of iron permeating a siliceous base, and shall be free from added impurities. It shall conform to the following requirements:

Color—Color Strength—Tone.—Equal to sample mutually agreed on by buyer and seller.

Table with 3 columns: Property, Maximum, Minimum. Rows include: Coarse particles: Retained on standard No. 200a screen (0.0, None), Iron oxide (None, 17), Lime (CaO) (5, None), Lead chromate (None, None), Organic colors (None, None).

a No. 200 screen is the same as screen formerly known as 200 mesh. 173047°-20

(b) PASTE.—Ocher in paste form shall consist of:

	Maximum	Minimum
	Per cent	Per cent
Pigment.....	71	69
Linseed oil.....	31	29
Moisture and volatile matter.....	0.5
Coarse particles and "skins" (total residue left on No. 200 screen) based on pigment.....	0.5

2. SAMPLING

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1000 packages be taken as representative of the whole.

With the dry pigment, this package shall be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test.

With the paste, whenever possible, an original unopened container shall be sent to the laboratory; and when this is for any reason not done, the inspector shall determine, by thorough testing with a paddle or spatula, whether the material meets the requirement regarding not caking in the container. (See 4 (a).) He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds. This sample shall be placed in a clean, dry, metal or glass container which it must nearly fill. The container shall be closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

Samples will, in general, be tested by the following methods, but the purchaser reserves the right to apply any additional tests, or use any available information to ascertain whether the material meets the specification.

3. LABORATORY EXAMINATION OF DRY PIGMENT

(a) COLOR AND TONE.—Weigh 1 g each of the color and standard and rub up separately on a glass plate or stone slab, using the same amount of bleached linseed oil in each case. Place portions of each side by side on a clean strip of glass, turn the glass over and compare the colors. Rubbing up (mixing with oil) is best done with a muller, and should be such that no lumps remain and that the consistency of both paste portions is the same. Smear (with the finger) portions of the pastes on a clear glass strip and compare the tone by transmitted light.

(b) COLOR STRENGTH.—Weigh accurately 0.05 g each of the color and standard and two portions of 1 g each of the zinc oxide. Add the color to one of the portions of zinc oxide and the standard to the other and rub up separately in linseed oil until on spreading out no dark streaks are visible. Place the color and standard tints side by side on a clean glass strip, turn the strip over and compare.

(c) COARSE PARTICLES.—Dry in an oven at 105 to 110° C a standard No. 200 brass or copper sieve, cool, and weigh accurately. Weigh 25 g of pigment which has been previously thoroughly dried by heating in an oven at 105 to 110° C until all moisture has been driven off. Transfer to a wide-mouth bottle or cylinder of about 300-cc capacity, add about 200 cc of dry kerosene, stopper, and shake vigorously for about 5 minutes. Remove the stopper and wash any pigment adhering to the stopper back into the cylinder with a jet of kerosene. Pour about 50 cc of the kerosene with suspended pigment onto the sieve, let drain through and gradually transfer the whole of the kerosene and pigment to the sieve, finally using a jet of kerosene to transfer the last of the pigment. With proper manipulation a large portion of the pigment will pass through the sieve during the process of transferring from the cylinder. When all pigment has been thrown on the sieve, wash with a jet of kerosene until no more pigment passes through. To make sure that all fine particles have been washed through, move the sieve from over the vessel, in which the main portion of kerosene and pigment has been caught, to over a clean glass dish resting on a white surface and wash all portions of the sieve with a jet of kerosene, using not less than 200 cc of kerosene. This kerosene caught in this dish should be entirely free from pigment. If any pigment can be seen in the liquid, repeat the washing until at least 200 cc can be washed through without showing any pigment. Then wash with a jet of kerosene all pigment adhering to the frame of the sieve beneath the wire mesh. Finally, wash the kerosene from the sieve with petroleum ether, dry the sieve at 105 to 110° C, cool, and weigh. The increase in weight should be not more than 0.005 g.

(d) MOISTURE.—Place 1 g of the sample in a wide-mouth, short weighing tube provided with a glass stopper, and weigh accurately. Heat with stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool and weigh. Calculate loss in weight as moisture.

(e) ORGANIC COLORING MATTER (A. S. T. M. "Standards," 1918, p. 656).—Test the pigment successively with hot water, 95 per

cent alcohol, alcoholic sodium hydroxide and acetic acid. Chloroform, sodium hydroxide, sulphuric acid, hydrochloric acid-stannous chloride solution, and other reagents may be tried. The solutions should remain colorless. The presence of an organic color may often be detected by the characteristic odor given off on ignition.

(f) TOTAL IRON OXIDE.—Ignite 1 g of the sample in a porcelain crucible at a dull red heat to destroy organic matter. Transfer to a 500 cc Erlenmeyer flask and add 20 cc of 1:1 hydrochloric acid. Digest just short of boiling until no dark specks can be seen in the insoluble residue. When the residue is light in color, the solution of iron may be considered complete. Dilute to 100 cc and without filtering, add 3 g of granulated zinc; put a funnel in the neck of the flask and heat when the action slackens; if basic iron salts separate out, add a few drops of hydrochloric acid. When the reduction is complete, add 30 cc of sulphuric acid (1:2) and as soon as the residual zinc is dissolved, wash down the funnel and neck of the flask with a fine jet of water. Now add 200 cc of cool water and 30 cc of titrating solution (see reagents) and titrate with standard potassium permanganate. Run a blank on the zinc and calculate ferric oxide (Fe_2O_3). Any other accurate method for determining iron may be used at the option of the analyst.

(g) TEST FOR LEAD AND CALCIUM BY THE USUAL QUALITATIVE METHODS.—If calcium is present in appreciable amount, determine it as follows: Ignite 2.5 g in a porcelain crucible at a dull red heat to destroy organic matter. Transfer to a 500 cc graduated flask; add 100 cc of 1:1 hydrochloric acid. Digest just short of boiling until no dark specks can be seen in the insoluble residue; add ammonia in slight excess and about 2 cc of hydrogen peroxide solution; cool, dilute to 500 cc; mix thoroughly, filter through a dry paper. Take 100 cc of the filtrate (corresponding to 0.5 g of sample), heat to boiling, add a few drops of ammonia and an excess of a hot saturated ammonium oxalate solution. Continue boiling until the precipitate becomes granular; let stand about 30 minutes, filter, wash with hot water until free from ammonium oxalate. Pierce the apex of the filter with a stirring rod and wash the precipitate into the beaker with hot water; pour warm dilute sulphuric acid (1:4) through the paper and wash a few times. Add about 30 cc of sulphuric acid (1:4), dilute to about 250 cc with hot water and titrate at once with standard potassium permanganate solution (the solution should not be below 60°C . when the end point is reached). Calculate to CaO. (The Fe value of $\text{KMnO}_4 \times 0.502 = \text{CaO}$ value.)

4. LABORATORY EXAMINATION OF THE PASTE

(a) **CAKING IN CONTAINER.**—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of ocher paste. The paste shall be finally thoroughly mixed, removed from the container, and the container wiped clean and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container and portions for the remaining tests promptly weighed out from it.

(b) **MIXING WITH OIL, OR THINNING.**—Add sufficient linseed oil to 100 g of the sample to make a liquid paint of proper consistency for application with a brush, noting the amount of oil necessary. Note the smoothness with which the paint works under the brush.

(c) **MOISTURE AND OTHER VOLATILE MATTER.**—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C for one hour, cool, and weigh. Calculate loss in weight as percentage of moisture and volatile matter.

(d) **PERCENTAGE OF PIGMENT.**—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until well settled. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc of extraction mixture and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C for two hours. Cool, weigh, and calculate the percentage of pigment.

(e) **EXAMINATION OF THE PIGMENT.**—Grind the pigment from (d) to a fine powder, pass through an 80-mesh sieve to remove any skins, preserve in a stoppered bottle, and examine as under 3(e), 3(f), and 3(g).

(f) **COLOR, TONE, AND COLOR STRENGTH.**—Extract the pigment from the vehicle with extraction mixture as in 4(d), except

that it is not necessary to accurately weigh the amount taken, and after washing with ether, dry in a vacuum at a temperature not above 70° C. Grind this extracted pigment fine enough to pass a No. 80 sieve to remove skins, and test as under 3(a) and 3(b).

(g) COARSE PARTICLES AND SKINS.—Weigh an amount of paste containing 25 g of pigment (see 4(d)), add 200 cc of kerosene, and wash through a No. 200 sieve as in 3(c). The residue remaining on the sieve should be not more than 0.125 g.

(h) PREPARATION OF FATTY ACIDS.—To about 25 g of the paste in a porcelain casserole, add 15 cc of aqueous sodium hydroxide (see reagents) and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add an excess of sulphuric acid of specific gravity 1.2 (8 to 10 cc will usually suffice), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer and insoluble mineral matter, wash once with water, then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off the water layer completely. Transfer the ether solution to a dry flask and add 25 to 50 g anhydrous sodium sulphate. Stopper the flask and let stand with occasional shaking at a temperature below 25° C until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution, if necessary, through a dry filter paper, into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a CaCl₂ tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C on a dry hot plate until the ether is entirely driven off. The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

NOTE. It is important to follow all of the details, since ether generally contains alcohol and after washing with water always contains water. It is very difficult to remove water and alcohol by evaporation from fatty acids, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

(i) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acids (h) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for 5 minutes, add 40 cc of water and mix; a clear solution indicates

that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(j) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of fatty acids (*h*) in a small weighing burette or beaker. Weigh accurately. Transfer, by dropping, about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to each of two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see Reagents) and let stand, with occasional shaking, for one-half hour. Add 10 cc of the 15 per cent potassium iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the difference between the average of the blank titrations and the titration on the sample, and the iodine value of the thiosulphate solution calculate the iodine number of the sample tested. (Iodine number is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

5. REAGENTS

(a) EXTRACTION MIXTURE.—

- 10 volumes ether (ethyl ether).
- 6 volumes benzol.
- 4 volumes methyl alcohol.
- 1 volume acetone.

(b) AQUEOUS SODIUM HYDROXIDE.—Dissolve 100 g of sodium hydroxide in distilled water and dilute to 300 cc.

(c) STANDARD SODIUM THIOSULPHATE SOLUTION.—Dissolve pure sodium thiosulphate in distilled water (that has been well boiled to free it from carbon dioxide) in the proportion of 24.83 g crystallized sodium thiosulphate to 1000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine. (See Treadwell-Hall, Analytical Chemistry, vol. 2, 3d ed., p. 646.) This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value, rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(d) STARCH SOLUTION.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(e) POTASSIUM IODIDE SOLUTION.—Dissolve 150 g of potassium iodide free from iodate in distilled water and dilute to 1000 cc.

(f) HANUS SOLUTION.—Dissolve 13.2 g of iodine in 1000 cc of 99.5 per cent glacial acetic acid, which will not reduce chromic acid. Add enough bromine to double the halogen content, determine by titration (3 cc of bromine is about the proper amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(g) ALCOHOLIC SODIUM HYDROXIDE SOLUTION.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1000 cc), kept at about 50° C for 15 days, and then distilled.

(h) POTASSIUM PERMANGANATE SOLUTION.—Dissolve 5.7 g of pure potassium permanganate in a liter of distilled water, let stand 8 to 14 days, siphon off the clear solution (or filter through an asbestos filter), and standardize as follows: In a 400 cc beaker dissolve 0.40 to 0.50 g of Bureau of Standards' sodium oxalate in 250 cc of hot water (80 to 90° C) and add 15 cc of dilute sulphuric acid (1:1). Titrate at once with the potassium permanganate solution, *stirring the liquid vigorously and continuously*. The permanganate must not be added more rapidly than 10 to 15 cc per minute, and the last 0.5 to 1 cc must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The solution should not be below 60° C by the time the end point is reached. (Too rapid cooling may be prevented by allowing the beaker to stand on a small asbestos covered hot plate during the titration. The use of a small thermometer as a stirring rod is most convenient). The weight of sodium oxalate used multiplied by 0.8334 gives its iron equivalent. The permanganate solution should be kept in a glass stoppered bottle painted black to keep out light.

(i) TITRATING SOLUTION.—Dissolve 160 g of manganese sulphate in water, dilute to 1750 cc, add 330 cc of orthophosphoric acid (specific gravity 1.72), and 320 cc of concentrated sulphuric acid.

WASHINGTON, April 1, 1920.