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UNITED STATES GOVERNMENT SPECIFICATION FOR
BASIC CARBONATE WHITE LEAD, DRY AND PASTE.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 5.

This Specification was officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by it.

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1. GENERAL.

Basic carbonate white lead may be ordered in the form of dry pigment or paste ground in linseed oil. Material shall be purchased by net weight.

(a) DRY PIGMENT.—The pigment shall be the product made from metallic lead and shall have a composition corresponding approximately to the formula $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. It shall be thoroughly washed after corroding, shall be free from impurities and adulterants, and shall meet the following requirements:

Color—Color strength.—When specified, shall be equal to that of a sample mutually agreed upon by buyer and seller.

	Minimum.	Maximum.
	Per cent.	Per cent.
Coarse particles retained on Standard No. 325 screen.....	1.0
Lead carbonate.....	65.0	75.0
Total impurities, including moisture.....	2.0

(b) PASTE.—The paste shall be made by thoroughly grinding the above-described pigment with pure raw or refined linseed oil.

The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Minimum.	Maximum.
	Per cent.	Per cent.
Pigment.....	90	92
Linseed oil.....	8	10
Moisture and other volatile matter.....	0.7
Coarse particles and "skins" (total residue retained on No. 325 screen based on pigment).....	1.5

NOTE.—Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages shall 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. 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.

Whenever possible, an original unopened container shall be sent to the laboratory with the paste; and when this is for any reason not done, the inspector shall determine by testing thoroughly with a paddle or spatula whether the material meets the requirement regarding not caking in the container. (See 4 (a).) After assuring himself that the paste is not caked, the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

3. LABORATORY EXAMINATION OF DRY PIGMENT.

(a) COLOR.—Take 1 g of the sample, add 10 to 12 drops linseed oil, rub up on a stone slab or glass plate with a flat-bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 1 g of the standard basic carbonate white lead. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as white or whiter than the "standard," it passes this test. If the standard is whiter than the sample, the material does not meet the specification.

(b) COLOR STRENGTH.—Weigh accurately 0.01 g of lampblack, place on a large glass plate or stone slab, add 5 drops of linseed oil, and rub up with a flat-bottomed glass pestle, or muller, then add exactly 10 g of the sample and 45 drops of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp-edge spatula and grind out two more times in a like manner, giving the pestle a uniform pressure. Treat another 0.01 g of the same lampblack in the same manner, except that 10 g of standard basic carbonate white lead is used instead of the 10 g of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light or lighter in color than the standard, it passes this test. If the standard is lighter in color than the sample, the material does not meet the specification.

(c) COARSE PARTICLES.¹—Dry in an oven at 105° to 110° C. a No. 325 screen, cool and weigh accurately. Weigh 25 g of the sample; dry at 100° C.; transfer to a mortar, add 100 cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene through the screen, breaking up all lumps, but not grinding. After washing with kerosene until all but the particles which are too coarse to pass the screen have been washed through, wash all kerosene from the screen with ether or petroleum ether, heat the screen for one hour at 105 to 110° C., cool and weigh.

(d) QUALITATIVE ANALYSIS.—Test for matter insoluble in acetic acid, zinc, calcium, etc., by the regular methods of qualitative analysis.

(e) MOISTURE.—Place 1 g of the sample in a tared wide-mouth short weighing tube provided with a glass stopper. Heat with

¹ For a general discussion of screen tests of pigments and data regarding many pigments on the market, see Circular No. 148 of the Educational Bureau, Scientific Section, Paint Manufacturers' Association of the United States.

stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool and weigh. Calculate loss in weight as moisture.

(f) TOTAL LEAD AND INSOLUBLE IMPURITY.—Weigh 1 g of the sample, moisten with water, dissolve in acetic acid. If any insoluble residue remains, filter, dry at 105 to 110° C. and weigh as insoluble impurity. Dilute the solution to about 200 cc, make alkaline with NH_4OH , then acid with acetic acid, heat to boiling and add 10 to 15 cc of a 10 per cent solution of sodium bichromate or potassium bichromate, and heat until the yellow precipitate assumes an orange color. Let it settle and filter on a Gooch crucible, washing by decantation with hot water until the washings are colorless, and finally transferring all the precipitate. Then wash with 95 per cent ethyl alcohol and then with ethyl ether; dry at 100° C. and weigh PbCrO_4 . Calculate to lead oxide ($\text{PbCrO}_4 \times 0.69 = \text{PbO}$). Total lead may be determined by the sulphate method if preferred.

(g) CARBON DIOXIDE.—Determine by evolution with dilute acid and absorption in soda-lime or KOH solution, calculate CO_2 to PbCO_3 , subtract PbO equivalent from total PbO and calculate residual PbO to Pb(OH)_2 .

$$\text{CO}_2 \times 6.072 = \text{PbCO}_3$$

$$\text{CO}_2 \times 5.072 = \text{PbO}$$

$$\text{PbO} \times 1.197 = \text{PbCO}_3$$

$$\text{PbO} \times 1.08 = \text{Pb(OH)}_2$$

4. LABORATORY EXAMINATION OF 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 white-lead paste. The paste shall finally be 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 thoroughly mixed paste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(b) MIXING WITH LINSEED OIL.—One hundred grams of the paste shall be placed in a cup, 30 cc linseed oil added slowly with

careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency.

(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 other volatile matter.

(d) PERCENTAGE OF PIGMENT.—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc “extraction mixture” (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, add enough 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 the 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 PIGMENT.—Grind the pigment from (d) to a fine powder, pass through a No. 80 screen to remove any “skins,” preserve in a stoppered tube and apply tests 3(a), 3(b), 3(d), 3(f), and 3(g).

(f) 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 lead sulphate precipitate, 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, add 25 to 50 g of 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 CaCl_2 tower) into the mouth of the Erlenmeyer flask and heat at a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

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.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(g) TEST FOR MINERAL OIL.—Place 10 drops of the fatty acid (f) in a 50 cc test tube, add 5 cc of alcoholic soda (see reagents), boil vigorously for five minutes, add 40 cc of water and mix. A clear solution indicates absence of more than a trace of unsaponifiable matter. If the solution is not clear, the oil is not pure linseed oil.

(h) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (f) 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 the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see reagents) and let it stand with occasional shakings 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 titration 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.

(i) COARSE PARTICLES AND "SKINS."—Weigh an amount of paste containing 25 g of pigment (see 4 (d)), add 100 cc kerosene, wash through a No. 325 screen and weigh the residue as in 3 (c).

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 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 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine.² 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 of boiling water, boil the mixture until the starch is practically dissolved, and then dilute to one liter.

(e) POTASSIUM IODIDE SOLUTION.—Dissolve 150 g potassium iodide free from iodate in distilled water and dilute to 1,000 cc.

(f) HANUS SOLUTION.—Dissolve 13.2 g iodine in 1,000 cc of glacial acetic acid, 99.5 per cent, which will not reduce chromic acid. Add enough bromine, about 3 cc to double the halogen content, which is determined by titration. The iodine may be dissolved by applying 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

² See Treadwell-Hall Analytical Chemistry, II, 3d ed., p. 646.

about 22 g per 1,000 cc. Let the solution 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 NaOH (about 80 g to 1,000 cc), kept at about 50° C. for 15 days, and then distilled.

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