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

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION NO. 6.

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.

CONTENTS.

1. GENERAL.

Basic sulphate 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 sublimed product prepared from lead sulphide ores, 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.
Coarse particles:	Per cent.	Per cent.
Retained on standard No. 325 screen		1.0
Composition:		
Lead oxide	11.0	18.0
Zinc oxide		9.0
Total impurities, including moisture		1.0
The remainder shall be lead sulphate.		

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(*b*) Pastes.—The paste shall be made by thoroughly grinding the dry 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. It shall mix readily in all proportions without curdling with linseed oil, turpentine, or volatile mineral spirits or any combination of these substances.

The paste shall consist of:

	Minimum.	Maximum.
	Per cent.	Per cent.
Pigment	89	91.0
Linseed oil	9	11.0
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.

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*.) After assuring himself that the paste is not caked in the container 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.

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.

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 sulphate white lead. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as white as 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 twice more 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 sulphate 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 as 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 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 acid ammonium acetate solution, for calcium, for carbonates, and for any other impurities suspected 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 stopper removed for two hours at a temperature between 100 and 105° C. Insert stopper, cool, and weigh. Calculate loss in weight as moisture.

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[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.

(*f*) INSOLUBLE IMPURITY AND TOTAL LEAD.—In a 250 cc beaker, moisten 1 g of the pigment with a few drops of alcohol; add 50 cc of acid ammonium acetate solution. (See Reagents 5*a*.) Heat to boiling and boil for 2 minutes. Decant through a filter paper, leaving any undecomposed matter in the beaker. To the residue in the beaker, add 50 cc of the acid ammonium acetate solution, heat to boiling, and boil for 2 minutes. Filter through the same paper and wash with hot water. If an appreciable residue remains, ignite and weigh as insoluble impurity. Unite the acid ammonium acetate solutions, heat to boiling, and add dropwise, with stirring, a slight excess (in total about 10 to 15 cc) of dichromate solution. (See Reagents 5*b*.) Heat until the precipitate assumes an orange color, let settle, filter on a weighed Gooch crucible, wash by decantation with hot water until the washings are colorless, and finally transfer all of the precipitate to the crucible. Then wash with 10 cc of 95 per cent ethyl alcohol and finally with 10 cc of ethyl ether. Dry at 110 to 120° C., cool, and weigh $PbCrO_4$. Calculate to PbO by multiplying by the factor 0.69.

(*g*) ZINC OXIDE.—Weigh accurately about 1 g of the pigment, transfer to a 400 cc beaker, add 30 cc of HCl (1:2), boil for 2 or 3 minutes, add 200 cc of water and a small piece of litmus paper, add NH_4OH until slightly alkaline, render just acid with HCl, then add 3 cc of concentrated HCl, heat nearly to boiling, and titrate with standard potassium ferrocyanide as in standardizing that solution. (See Reagents 5*d*.) Calculate total zinc as ZnO.

(*h*) LEAD SULPHATE.—Treat 0.5 g of the pigment in a 400 cc beaker with a few drops of alcohol, add 10 cc of bromine water, 10 cc of HCl (1:1), and 3 g of NH_4Cl. Cover with a watch glass and heat on a steam bath for 5 minutes, add hot water to give a total volume of about 200 cc, boil for 5 minutes, filter to separate any insoluble matter (a pure pigment should be completely dissolved), and wash thoroughly with hot water. (The insoluble matter may be ignited, weighed, and examined qualitatively.) Neutralize the clear solution (original solution or filtrate from insoluble matter) in a covered beaker with dry Na_2CO_3, add 1 g more of dry Na_2CO_3, and boil 10 to 15 minutes. Wash off cover, let settle, filter, and wash with hot water. Redissolve the precipitate in HCl (1:1), reprecipitate with Na_2CO_3 as above, filter, and wash thoroughly with hot water. Acidify the united filtrates with HCl, adding about 1 cc in excess. Boil to expel bromine, and to the clear boiling solution add slowly with stirring 15 cc of barium chloride solution. (See Reagents 5*e*.) Let stand on steam bath for about one hour, filter on a weighed Gooch crucible, wash thoroughly with boiling water, dry, ignite, cool, and weigh as $BaSO_4$. Calculate to $PbSO_4$, using the factor 1.3.

(*i*) CALCULATIONS.—Calculate the percentage of $PbSO_4$ to PbO by multiplying by the factor 0.736 and subtract the result from the percentage of PbO found under (*f*); report the difference as PbO. Report ZnO found under (*g*) as percentage of ZnO. Moisture and insoluble matter are reported as such.[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 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 the portions for the remaining tests promptly weighed out from it.

(*b*) MIXING WITH LINSEED OIL.—One hundred grams of the paste shall be placed in a cup, and 30 cc of 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 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,

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[2] A method given by Schaeffer, J., Ind. and Eng. Chem., 6, p. 200 (1914), based on calculation of composition after determination of moisture, impurities, total lead, and total zinc oxide, is sometimes used. This method requires very accurate determination of Pb and ZnO, since the errors of determination are multiplied by approximately four in making the calculation to PbO and Pbso4.

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 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 examine as under 3 (*a*), 3 (*b*), 3 (*d*), 3 (*f*), 3 (*g*), 3 (*h*), and 3 (*i*), Laboratory Examination of Dry Pigment.

(*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 1 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 $PbSO_4$ 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 violently, so as to avoid forming 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 completely the water layer. 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 $CaCl_2$ 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.[3]

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[3] 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.

(*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 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.

(*h*) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*f*) in a small weighing burette or beaker and 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 and 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 5*k*) 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 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 out an amount of paste containing 25 g of pigment (see *d*), add 100 cc of kerosene, wash through No. 325 screen, and weigh the residue as in 3 (*c*).

5. REAGENTS.

(*a*) ACID AMMONIUM ACETATE SOLUTION.—Mix 150 cc of 80 per cent acetic acid, 100 cc of water, and 95 cc of strong ammonium (specific gravity 0.90).

(*b*) DICHROMATE SOLUTION.—Dissolve 100 g sodium dichromate ($Na_2Cr_2O_7 2H_2O$) or potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1,000 cc.

(*c*) URANYL INDICATOR FOR ZINC TITRATION.—A 5 per cent solution of uranyl nitrate in water or a 5 per cent solution of uranyl acetate in water made slightly acid with acetic acid.

(*d*) STANDARD POTASSIUM FERROCYANIDE.—Dissolve 22 g of the pure salt in water and dilute to 1,000 cc. To standardize, transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure ZnO to a 400 cc beaker. Dissolve in 10 cc of HCl and 20 cc of water. Drop in a small piece of litmus paper, add NH_4OH until slightly alkaline, then add HCl until just acid and finally add 3 cc of strong HCl. Dilute to about 250 cc with hot water and heat nearly to boiling. Run in the ferrocyanide solution slowly from a burette with constant stirring until a drop tested on a white porcelain plate with a drop of the uranyl indicator shows a brown tinge after standing 1 minute. A blank should be run with the same amounts of reagents and water as in the standardization. The amount of ferrocyanide solution required for the blank should be subtracted from the amounts used in standardization and in titration of the sample. The standardization must be made under the same conditions of temperature, volume and acidity as obtain when the sample is titrated.

(*e*) BARIUM CHLORIDE SOLUTION.—Dissolve 100 g of pure crystallized barium chloride in water and dilute to 1,000 cc.

(*f*) STANDARD SODIUM THIOSULPHATE SOLUTION.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from CO_2 in the proportion of 24.83 g of 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. (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 strength. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(*g*) 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, and boil the mixture until the starch is practically dissolved; then dilute to 1 liter.

(*h*) EXTRACTION MIXTURE.—Mix 10 volumes ether (ethyl ether), 6 volumes benzol, 4 volumes methyl alcohol, and 1 volume acetone.

(*i*) AQUEOUS SODIUM HYDROXIDE.—Dissolve 100 g of NaOH in distilled water and dilute to 300 cc.

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

(*k*) HANUS SOLUTION.—Dissolve 13.2 g of iodine in 1,000 cc of glacial acetic acid, 99.5 per cent, which will not reduce chromic acid. Add enough bromine to double the halogen content, determined 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.

(*l*) ALCOHOLIC SODIUM HYDROXIDE SOLUTION.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 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; 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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