DEPARTMENT OF COMMERCE

CIRCULAR

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 85

RECOMMENDED SPECIFICATION FOR BASIC SULPHATE WHITE LEAD, DRY AND PASTE

Prepared and recommended by the U. S. Interdepartmental Committee on Paint Specification Standardization, September 22, 1919. P. H. Walker, Bureau of Standards, Chairman; H. E. Smith, U. S. Railroad Administration, Secretary

ISSUED JANUARY 26, 1920

PRICE, 5 CENTS
Sold by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1920

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PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, SEPTEMBER 22, 1919. P. H. WALKER, BUREAU OF STANDARDS, CHAIRMAN; H. E. SMITH, U. S. 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 this specification to a number of representatives of the paint and varnish industry, including all of the large manufacturers of white lead, and gave careful consideration to the replies received in time)

CONTENTS

cc kerosene, thoroughly mix by gentle pressure with a pestle to break up all lumps, wash with kerosene first through the 200 and then through the 325 sieve, breaking up all lumps but not grinding. After washing with kerosene until all but the particles too coarse to pass the sieves have been washed through, wash all kerosene from the sieves with ether or petroleum ether, heat the sieves for one hour at 105 to 110° C, cool, and weigh. The increase in weight of the No. 200 sieve should be not more than 0.010 g, and of the No. 325 sieve not more than 0.500 g.

(*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 2 hours at a temperature between 100 and 105° C. Insert stopper, cool, and weigh. Calculate loss in weight as moisture.

(*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 5e.) Let stand on steam bath for about 1 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.[1]

IV. 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

[1] 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 $PbSO_4$.

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 1 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, 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 2 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.[2]

(*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 centi-

[2] 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.

grams 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 100 g of pigment (see *d*), add 100 cc of kerosene, wash through No. 325 screen, and weigh the residue as in 3 (*c*). The total residue left on the screen should be not more than 0.5 g.

V. REAGENTS

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

(*b*) DICHROMATE SOLUTION.—Dissolve 100 g sodium dichromate ($Na_2Cr_2O_72H_2O$) or potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1000 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 1000 cc. To standadize, 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 substracted 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 1000 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 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 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 methly 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 1000 cc.

(*k*) HANUS SOLUTION.—Dissolve 13.2 g of iodine in 1000 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 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; it will keep colorless longer if the alcohol is previously treated with NaOH (about 80 g to 1000 cc) kept at about 50°C for 15 days, and then distilled.

WASHINGTON, September 30, 1919.