

DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

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RECOMMENDED SPECIFICATIONS FOR RED LEAD,  
DRY AND PASTE

PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, JANUARY 26, 1920; 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 the specifications to a large number of representatives of the paint manufacturers, including the manufacturers of red lead, and gave careful consideration to the replies received.]

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1. GENERAL

Red lead may be ordered in the form of dry pigment or of paste ground in pure raw linseed oil. Two grades of pigment, known as 85 and 95 per cent, may be ordered, and each contract shall state which grade is desired.<sup>1</sup>

Material shall be bought by net weight.

<sup>1</sup> Avoid storing red-lead paste in places of high temperature, as heat accelerates the tendency of this material to cake or harden.

Purchasers are cautioned not to buy red lead in paste form unless it is to be used within three months after shipment by the contractor.

(a) DRY PIGMENT.—The pigment shall consist entirely of oxides of lead free from all adulterants and shall meet the following requirements:

	85 per cent grade	95 per cent grade
True red lead ( $Pb_3O_4$ ), not less than.....	Per cent 85	Per cent 95
Total impurities, including moisture, soluble matter, water—and matter insoluble in a mixture of nitric acid and hydrogen peroxide, not more than.....	1	1
Remainder shall be lead monoxide ( $PbO$ ).		
Coarse particles: Retained on standard No. 200 <sup>a</sup> screen, not more than.....	0.3	0.3

<sup>a</sup> The No. 200 screen is the same as the screen formerly known as 200-mesh.

When mixed with raw linseed oil, turpentine, and liquid drier in the proportion

Dry red lead.....	pounds..	20
Raw linseed oil.....	pints..	5
Turpentine.....	gills..	2
Liquid drier.....	do....	2

the resulting paint when brushed on a smooth vertical iron surface shall dry hard and elastic without running, streaking, or sagging.

(b) PASTE.—The paste shall be made by thoroughly grinding the specified grade of dry pigment with pure raw or refined linseed oil.

The paste, as shipped by the contractor, and for three months thereafter, shall not be caked in the container and shall readily break up in oil to form a smooth paint of brushing consistency. The paste shall have the following composition:

	Maximum	Minimum
Pigment.....	Per cent 94	Per cent 92
Linseed oil.....	8	6
Moisture and other volatile matter.....	0.5	.....
Coarse particles and skins (total residue left on No. 200 screen).....	0.5	.....

When mixed with raw linseed oil, turpentine, and liquid drier in the proportions

Red lead paste.....	pounds..	20
Raw linseed oil.....	pints..	4½
Turpentine.....	gills..	2
Liquid drier.....	do....	2

the resulting paint when brushed on a smooth vertical iron surface shall dry hard and elastic without running, streaking, or sagging.

## 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 is to 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.

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 thoroughly 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 can, 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.

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, DRY PIGMENT

(a) **QUALITATIVE ANALYSIS.**—Follow ordinary methods of qualitative analysis. The material should give a negative test for matter insoluble in a mixture of nitric acid and hydrogen peroxide, and material other than oxides of lead. (If more than a faint cloud remains after treatment with nitric acid and hydrogen peroxide, it will be necessary to take a weighed sample and determine the percentage of this insoluble matter.) Boil 2 g of the sample with 25 cc of 95 per cent ethyl alcohol, let settle, decant off the supernatant liquid, boil the residue with water, decant as before, and boil the residue with very dilute ammonia. If the alcohol, water, or ammonia are colored, organic coloring matter is indicated, which is cause for rejection.

(b) **TRUE RED LEAD.**—Weigh accurately 1 g of the sample into a 200 cc Erlenmeyer flask, add a few drops of distilled water, and rub the mixture to a smooth paste with a glass rod flattened on

the end. Mix in a small beaker 30 g of pure crystallized sodium acetate, 2.4 g of pure potassium iodide, 10 cc of water, and 10 cc of 50 per cent acetic acid. Stir until all is liquid, warm gently, and, if necessary, add 2 to 3 cc more water. Cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved, add 30 cc of water containing 5 to 6 g of sodium acetate, and titrate at once with standard sodium thiosulphate solution, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub any undissolved particles up with the rod until free iodine no longer forms, wash off the rod, and add the sodium thiosulphate solution until pale yellow. Add starch solution and titrate until colorless, add standard iodine solution until the blue color is just restored. From the amount of standard iodine solution used, calculate the correction to be applied to the thiosulphate reading, and calculate true red lead (iodine value of thiosulphate  $\times 2.7 = \text{Pb}_3\text{O}_4$  value).

(c) WATER SOLUBLE MATTER.—Digest 10 g of the sample with 200 cc of hot water on a steam bath for 1 hour; filter and wash with hot water until no residue is left on evaporating a few drops of the washings. Evaporate the filtrate to dryness in a weighed dish on a steam bath, heat for 30 minutes at 105 to 110° C, cool, and weigh.

(d) COARSE PARTICLES.—Dry a standard No. 200 brass or copper sieve in an oven at 105 to 110° C, cool, and weigh accurately. Weigh 50 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 five minutes. Remove the stopper and, with a jet of kerosene, wash back into the cylinder any pigment adhering to the stopper. Pour about 50 cc of the kerosene with suspended pigment on to 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 particles have been thoroughly 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 0.150 g.

(e) RUNNING, STREAKING, OR SAGGING.—Mix paint and apply as per specifications. About the smallest amount that can be conveniently made up will be 154 g dry red lead, 40 cc raw linseed oil, and 4 cc each of turpentine and liquid drier.

#### 4. LABORATORY EXAMINATION, 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 red-lead paste. The paste shall finally be thoroughly mixed, removed from the container, 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.

(b) MIXING WITH LINSEED OIL, RUNNING, STREAKING, AND SAGGING.—Mix as per specification to a paint, first using only the linseed oil and noting whether the paste breaks up readily and the resulting mixture is smooth. About the smallest amount that can be conveniently made up will be 154 g red-lead paste, 36 cc raw linseed oil, and 4 cc each of turpentine and liquid drier.

(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 the 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 clear. 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 percentage of pigment.

(e) EXAMINATION OF PIGMENT.—Grind the pigment from (d) to a fine powder, pass through a No. 80 sieve to remove any "skins," preserve in a stoppered tube, and apply tests 3 (a), 3 (b), and 3 (c).

(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 water and 50 cc 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 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 CaCl<sub>2</sub> 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.

(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 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. 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 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.

(i) COARSE PARTICLES AND SKINS.—Weigh an amount of paste containing 50 g of pigment (see 4(*d*)), add 200 cc of kerosene, and wash through a No. 200 sieve as in 3(*d*). The residue remaining in the sieve shall not be more than 0.25 g.

## 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 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. 11, 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 solda 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, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(e) STANDARD IODINE SOLUTION.—Dissolve 13 g of resublimed iodine and 18 g of pure potassium iodide (free from iodates) in 50 cc of distilled water, and dilute to 1000 cc. Determine its exact value by titrating with the standard sodium thiosulphate solution.

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

(g) 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, 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.

(h) 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.

WASHINGTON, February 7, 1920.