

# DEPARTMENT OF COMMERCE

## BUREAU OF STANDARDS

S. W. STRATTON, Director

### CIRCULAR OF THE BUREAU OF STANDARDS

No. 94

[April 21, 1920,]

## RECOMMENDED SPECIFICATION FOR BLACK PAINT, SEMIPASTE AND READY-MIXED

PREPARED AND RECOMMENDED BY THE U. S. INTERDEPARTMENTAL COMMITTEE ON PAINT SPECIFICATION STANDARDIZATION, MARCH 22, 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 specification to a large number of paint manufacturers and gave careful consideration to the replies received.]

### CONTENTS

	Page
1. General .....	1
2. Sampling .....	3
3. Laboratory examination—Semipaste .....	3
4. Analysis of pigment .....	6
5. Laboratory examination—Mixed paint .....	7
6. Reagents .....	8

### 1. GENERAL

Black paint may be ordered in the form of either semipaste paint or ready-mixed paint.

The basis of purchase may be either by net weight or by volume (231 cubic inches to the gallon).

(a) PIGMENT.—The pigment in both semipaste and ready-mixed paints shall consist of carbon, lead oxide, insoluble siliceous material, and, at the option of the manufacturer, oxide of iron. The pigment shall show on analysis not less than 20 per cent of carbon and not less than 5 per cent of lead oxide calculated as

$Pb_3O_4$ . The total of the lead oxide, iron oxide, insoluble siliceous material, and loss on ignition shall be not less than 99 per cent.

(b) LIQUID.—The liquid in semipaste paint shall be entirely pure raw or refined linseed oil; in ready-mixed paint it shall contain not less than 80 per cent pure raw linseed oil, the balance to be combined drier and thinner. The thinner shall be turpentine, volatile mineral spirits, or a mixture thereof.

(c) SEMIPASTE.—Semipaste shall be made by thoroughly grinding the pigment with pure raw or refined linseed oil.

The semipaste as received and three months thereafter shall be not caked in the container and shall break up readily in linseed oil to form a smooth paint of brushing consistency. It shall mix readily with linseed oil, turpentine, or volatile mineral spirits, or any combination of these substances, in all proportions without curdling. The color and hiding power when specified shall be equal to that of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 10.0 pounds. The paste shall consist of:

	Maximum	Minimum
	Per cent	Per cent
Pigment.....	52	48
Linseed oil.....	52	48
Moisture and other volatile matter.....	0.7	.....
Coarse particles and "skins" (total residue retained on No. 200 screen based on pigment) <sup>a</sup> .....	0.5	.....

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

(d) READY-MIXED PAINT.—Ready-mixed paint shall be well ground, shall not settle badly or cake in the container, shall be readily broken up with a paddle to a smooth uniform paint of good brushing consistency, and shall dry within 18 hours to a full oil gloss, without streaking, running, or sagging. The color and hiding power when specified shall be equal to those of a sample mutually agreed upon by buyer and seller. The weight per gallon shall be not less than 9 pounds. The paint shall consist of:

	Maximum	Minimum
	Per cent.	Per cent.
Pigment.....	32	28
Liquid (containing at least 80 per cent linseed oil).....	72	68
Water.....	0.5	.....
Coarse particles and "skins" (total residue retained 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 shall be taken as representative of the whole. 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 caking in the container. He shall then thoroughly mix the contents of the container and draw a sample of not less than 5 pounds of the thoroughly mixed paint, place it in a clean, dry metal or glass container, which it shall 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—SEMIPASTE

(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 than a normal good grade of semipaste paint. The semipaste 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 semipaste shall be placed in a clean container and the portions for the remaining tests promptly weighed out.

(b) **COLOR.**—Place some of the paint on a clean clear glass plate. Place some of the standard agreed upon beside the sample on the plate, turn the glass over, and compare the colors.

(c) **WEIGHT PER GALLON.**—From the weight of a known volume of the paste calculate the specific gravity, which multiplied by 8.34 gives the weight in pounds per gallon. Any suitable container of known volume may be used for the purpose, but a short cylinder of heavy glass with rounded bottom about 75 mm high

and having a capacity of from 125 to 175 cc (a glass cap to keep dust from reagent bottle stopper) is a convenient apparatus for the purpose. The capacity of this vessel is determined to within 1 cc. The paste is packed into it until completely full, the top leveled off smooth with a spatula, and weighed to  $\pm 0.5$  g. Subtract the weight of the empty container and divide the remainder by the number of cubic centimeters representing the capacity of the container. The quotient is the specific gravity, which can be thus determined within  $\pm 2$  in the second decimal place.

(d) MIXING WITH LINSEED OIL.—One hundred grams of the paste shall be placed in a cup, 70 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.

(e) 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.

(f) 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. Grind the pigment to a fine powder, pass through a No. 80 sieve to remove any skins, and preserve in a stoppered bottle.

(g) 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, 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 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<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.

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.

(h) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acid (*g*) 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.

(i) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (*g*) in a small weighing burette or beaker. Weigh accurately. Transfer by dropping about 0.15 g (0.10 to 0.20 g) into a 500 cc bottle having a well-grounded 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 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.

(j) COARSE PARTICLES AND SKINS.—Dry in an oven at 105 to 110° C a No. 200 sieve, cool, and weigh accurately. Weigh an amount of semipaste containing 30 g of pigment (see 3 (f)), add 50 cc of kerosene, mix thoroughly, and wash with kerosene through the sieve, breaking up all lumps but not grinding. After washing with kerosene until all but the particles too coarse to pass the sieve have been washed through, wash all kerosene from the sieve with ether or petroleum ether, heat the sieve for one hour at 105 to 110° C, cool, and weigh. The total residue left on the sieve should be not more than 0.15 g.

#### 4. ANALYSIS OF PIGMENT

(a) QUALITATIVE ANALYSIS.—Make qualitative analysis following ordinary methods.

(b) LOSS ON IGNITION.—Ignite 1 g of the pigment in a weighed porcelain crucible until all carbon is consumed. It is best to use gentle heat with free access of air. Cool, weigh, and calculate the percentage of loss on ignition.

(c) CARBON AND INSOLUBLE SILICEOUS MATERIAL.—Place 1 g of the pigment in a porcelain dish, moisten with a few drops of alcohol, add 20 cc of concentrated hydrochloric acid, cover, and heat on steam bath for 15 minutes. Remove cover and evaporate to dryness, moisten with hydrochloric acid, add 25 cc of water, filter on a weighed Gooch crucible, and wash with hot water until the washings are free from lead and iron. Dry the crucible and contents at 105 to 110° C for 2 hours. Ignite for 7 minutes in a current of dry carbon dioxide (using a Rose crucible cover) with a flame about 20 cm high. Cool in a current of dry carbon dioxide and weigh. Then ignite with free access of air (or in a current of oxygen) until all carbon is consumed. Cool and weigh. The loss in weight is calculated as carbon, and the residue remaining on the Gooch crucible is calculated as insoluble siliceous material,

unless barium sulphate has been found by qualitative test. The presence of barium sulphate is cause for rejection.

(d) LEAD OXIDE AND IRON OXIDE.—Determine lead and iron in the filtrate from the carbon determination by any convenient method, calculating lead to  $Pb_3O_4$  and iron to  $Fe_2O_3$ .

#### 5. LABORATORY EXAMINATION—MIXED PAINT

(a) CAKING IN CONTAINER.—Follow the procedure outlined in 3(a), noting that the paint should be no more difficult to break up than a good grade of mixed paint.

(b) COLOR.—Follow the procedure outlined in 3(b).

(c) WEIGHT PER GALLON.—Weigh a clean, dry, 100-cc graduated flask. Fill to the mark with the thoroughly mixed paint and weigh again. The increase in weight expressed in grams, divided by 100, gives the specific gravity, which multiplied by 8.34 gives the weight in pounds per gallon.

(d) BRUSHING PROPERTIES AND TIME OF DRYING.—Brush the well-mixed paint on a suitable panel, which may be ground glass, steel, or well-filled wood. Note whether the paint works satisfactorily under the brush. Place the panel in a vertical position in a well-ventilated room and let stand for 18 hours. The paint shall be dry, smooth, and free from streaks.

(e) WATER.—Mix 100 g of the paint in a 300-cc flask with 75 cc of toluol. Connect with a condenser and distill until about 50 cc of distillate has been collected in a graduate. The temperature in the flask should be then about 105 to 110° C. The number of cubic centimeters of water collecting under the toluol in the receiver is the percentage of water in the paint. Material complying with the specification should yield less than 0.5 cc.

(f) VOLATILE THINNER.—Follow the procedure outlined in 3(e). Correct the result for any water found (see 5(e)) and report the remainder as volatile thinner.

(g) PERCENTAGE OF PIGMENT.—Follow the procedure outlined in 3(f).

(h) TESTING NONVOLATILE VEHICLE.—Follow the procedure outlined in 3(g), 3(h), and 3(i), except that in the preparation of the fatty acids the mixture of paint and alkali is heated on the steam bath until all volatile thinner is driven off.

(i) COARSE PARTICLES AND SKINS.—Follow the procedure outlined in 3(j).

(j) TESTING PIGMENT.—Follow the procedure outlined in 4(a) to 4(d) inclusive.

## 6. 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. 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, 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.

(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.

WASHINGTON, March 22, 1920.