

(June 29, 1933)

SUGGESTED SPECIFICATION FOR COLD WATER PAINT,
CASEIN TYPE

Abstract

This paper briefly describes three commonly used types of casein binder cold water paints. A specification based on tests of a number of commercial paints is suggested for trial by any large users of such material.

A class of paints known as cold water paints, in which casein is used as the binder, has been in use for a considerable period of time. As early as 1910 Scott¹ published formulas for these paints in which zinc oxide

1. "White Paints and Painting Materials", by W.G.Scott, The Modern Painter, Chicago, U.S.A. (1910).

was the sole pigment. Most generally, however, whiting, with or without cheap white extending pigments such as china clay, was used. Coloring was accomplished by adding lime-proof pigments such as iron oxide, chromium oxide, ultramarine blue, etc. In order to disperse or dissolve the finely ground casein when water was added, hydrated lime was introduced. In addition, small amounts of alkaline salts such as borax, trisodium phosphate, etc., were often incorporated into the paint mixture to hasten or to complete the dispersing or solvent action of the free lime on the casein. Sometimes small amounts of other materials, intended to retard or to prevent the decay of casein, were added.

These cold water paints were marketed in powder form and were prepared for use by mixing or stirring with water. Early in 1928 cold water paints appeared on the market in the form of water pastes. These paints contained true hiding pigments which caused them to be more opaque when the film was wet than was the case with the older powder type. About June, 1931, the powder paints first appeared with opaque pigments.

This Bureau began testing samples of the new type of paste cold water paints in June 1929, and somewhat later (September 1931) samples of the new type of dry powder paints were also received for test. However, it was not until 1932 that a large number of samples of both kinds were received from Government Departments. Approximately one hundred samples were tested in 1932 and the early part of 1933. The tests gave information as to the chemical and physical characteristics of these paints. No information as to the important property of durability was obtained. The tests did show that, in the case of paste cold water paints, considerable difficulty was experienced by many manufacturers in keeping their products stable in the package. One brand of paint was found to be very stable. For example, thirty-two months after receipt this material was still free from settling or deterioration in the package. On the other hand, many samples of other brands showed bad settling in the can, granulation, thinning, or decomposition of the cascine (putrid odor), within one or two months after receipt of the samples. However, in recent months, a noticeable improvement has occurred in the stability of these paste water paints. Manufacturers undoubtedly are learning how to stabilize and preserve their products.

In the latter part of 1932, several of the more progressive manufacturers requested the Bureau of Standards to prepare standard Federal Specifications for these paints. However, since so little is known about the service that can be expected from them, it seemed more advisable to issue simply a suggested specification for trial by various users. Accordingly a draft of such a specification was sent to a number of interested manufacturers, and later was printed in the February 1933 number of *Drugs, Oils and Paints*. After considering many comments received on this tentative specification and after conferences with interested manufacturers, as well as Governmental users, the following specification is suggested for trial.

SUGGESTED SPECIFICATION FOR

PAINT, COLD WATER, CASEIN BINDER, WHITE AND LIGHT TINTS

A. NOTE

This is not a Federal specification, but is suggested for trial by any large user of casein cold water paint. Casein cold water paints, especially for exterior use, are not intended to be as durable as good oil paints. However, there is a definite field for this type of low-priced paint, for certain exterior surfaces and particularly for interior use. Where the combination of extreme dampness and poorly lighted conditions is present, the use of cement water paint may be preferable. Casein paint is particularly suitable for the decoration of plaster and other dry interior masonry surfaces.

B. GRADES AND TYPES

B-1. This specification covers two grades and two types of paint as follows:

Grade A -- Whiting grade, dry powder.

Grade B -- Zinc sulphide, titanium oxide grade.

Type 1 -- Dry powder

Type 2 -- Paste

(The grade or grades and type or types desired shall be stated in the invitation for bids.)

C. MATERIAL

C-1. The material shall be as specified under Detail Requirements.

D. GENERAL REQUIREMENTS

D-1. Basis of purchase. -- Grade A and Grade B, Type 1, casein binder cold water paint shall be purchased by net weight. Grade B, Type 2, shall be purchased by volume (231 cu. in. at 15.5°C (60°F) equals 1 gallon.)

D-2. Application. -- When so stated on the package, the materials shall be mixed and applied in strict accordance with the manufacturer's printed directions. The user and the testing laboratory should be furnished with such directions. However, the amounts of water to add to a given grade of material shall very closely approximate those given in paragraphs E-1-b, E-2-b, and E-3-b.

E. DETAIL REQUIREMENTS

E-1. Grade A.-

E-1-a. Composition.- Grade A cold water paint shall consist of a finely ground, uniform mixture of a good grade of a suitable easily dispersed, light weight white pigment, such as whiting or other suitable fillers, free lime, and casein with a suitable non-poisonous preservative. When necessary to produce the required tint, lime-proof colors, such as ochers, umber, sienna, lampblack, chrome oxide green and iron oxide red and brown may be added.

It must yield on analysis:

	Maximum per cent	Minimum per cent
Commercial casein (nitrogen factor 7.7)	--	10.0
Free lime (computed as Ca(OH) ₂)	15.0	10.0

E-1-b. Physical and working properties (See also D-2).-

The material shall be in powder form, free from any lumps that are not easily friable, and shall readily mix with water at 70°F in the proportion of 8 to 10 lbs. of powder to 4 quarts (See D-2) of water to form, after thoroughly stirring several times during a period of 30 minutes, a paint of good brushing consistency of smooth texture showing no undissolved particles of casein. When applied to wood, plaster, brick or cement it shall set to touch within 2 hours and dry within 18 hours to a smooth, non-rubbing, uniform flat finish that is either white or of a color matching that of an agreed upon sample. With white paint the reflection of the dry film shall be not less than 80% (relative to magnesium oxide). After five days of drying, marks made with a soft lead pencil (No.2) shall be easily removable by careful washing with a sponge, dampened with soapy water without appreciably marring the surface, and black cloth shall not be soiled by gentle rubbing on the dry paint film. The above mixture of water and powder after standing for 18 hours must be capable of being easily remixed and must not have an offensive odor.

NOTE.- While the paint should meet this mixing requirement, casein cold water paint should always be used the same day that it is mixed.

E-2. Grade B, Type 1.-

E-2-a. Composition.- Grade B, Type 1, cold water paint shall be a dry powder consisting of a uniform mixture of either light-proof lithopone, titanium pigment, zinc sulphide or any mixture thereof, together with extenders (such as clay,

whiting, or similar materials), casein, with suitable casein solvents, and a non-poisonous preservative, and suitable lime-proof tinting materials when required.

It must yield on analysis:

	Maximum per cent	Minimum per cent
Commercial casein (nitrogen factor 7.7)	--	10.0
Sum of zinc sulphide (ZnS) and titanium dioxide (TiO ₂)	--	15.0

(The zinc sulphide and titanium dioxide may be either light-proof lithopone, titanium pigment, zinc sulphide or a mixture thereof, provided the sum of the zinc sulphide (ZnS) and titanium dioxide (TiO₂) is not less than 15.0 per cent by weight of the total material.)

E-2-b. Physical and working properties.- The material shall be in powder form free from any lumps that are not easily friable and shall mix satisfactorily with water at 70°F, and the casein, lime, and any other solvent for the casein present shall be so finely ground that after thoroughly stirring several times during a period of 30 minutes the paint shall be of a smooth texture showing no undissolved particles of casein. When properly mixed with water in the proportion of about ten pounds of powder to four to five quarts of water and, if the manufacturer so directs, one pint of linseed oil, there shall result a smooth paint of good brushing consistency, that will set to touch within two hours and dry within 18 hours to a smooth, uniform, opaque flat finish that is non-yellowing, is not darkened by light and is non-rubbing. It shall dry sufficiently under normal conditions so that two coats may be applied the same day. The white paint shall show a high reflection value (at least 84 per cent relative to magnesium oxide). After five days of drying, marks made with a soft lead pencil (No.2) shall be easily removable by careful washing with a sponge, dampened with soapy water, without appreciably marring the surface, and black cloth shall not be soiled by gentle rubbing on the dry paint film. The mixed cold water paint shall be capable of remixing readily at the end of 18 hours, and shall not have an offensive odor. See note at the end of E-1-b.

E-3. Grade B, Type 2.-

E-3-a. Composition.- Cold water paste paint shall consist of either light-proof lithopone, titanium pigment, zinc sulphide or any mixture thereof with or without extenders (such as clay, whiting or similar materials) and lime-proof tinting materials when required, intimately mixed in a vehicle consisting of casein thoroughly dissolved in suitable solvents, with a non-poisonous preservative added (compounds of mercury shall be absent) if necessary.

It shall show on analysis:

	Maximum per cent	Minimum per cent
Total loss at 105 to 110°C (water)-----	35.0	--
Commercial casein (nitrogen factor 7.7) computed on non-volatile matter (total solids) -----	--	10.0
Sum of zinc sulphide (ZnS) and titanium dioxide (TiO ₂) computed on non-volatile matter (total solids) -----	--	15.0

E-3-b. Physical and working properties.- The material shall be a smooth, uniform paste. Any appreciable separation of liquid above the paste, caking, granulation or hardening in the container, or offensive odor, either when received or within six months thereafter, will be cause for rejection. It shall be easily mixed with one-half its volume of water at 70°F or, when the manufacturer so advises, with one-half its volume of a mixture of hydrated lime and water, provided that the amount of hydrated lime shall not exceed 7 ounces per gallon of paste, to a paint of good brushing consistency which will set to touch within 2 hours and dry within 18 hours to a smooth, uniform, opaque flat finish that is non-yellowing and non-rubbing, of good hiding power and, if the paint is white, of high reflecting value (at least 84 per cent relative to magnesium oxide). The mixed cold water paint shall be capable of remixing readily after standing 18 hours and shall not then have an offensive odor. See note at the end of E-1-b.

After the paint has been mixed and applied according to the manufacturer's directions and then allowed to dry for five days marks made with a soft lead pencil (No. 2) shall be easily removable by careful washing, and black cloth shall not be soiled by gentle rubbing on the dry paint film.

F. METHODS OF INSPECTION, SAMPLING AND TESTING

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

F-1. Inspection.- The inspector shall take a single container out of each lot of not more than 1000 pounds as representative of the whole. He shall open the container and carefully note condition of contents. With powder products (Grade A and Grade B, Type 1), if the material is in hard lumps that are not easily friable, or if it has a pronounced disagreeable (putrid) odor, or if the color is obviously different from the agreed upon standard, the shipment shall be rejected without further test. With the paste product (Grade B, Type 2), if this material is not a smooth paste, showing no appreciable separation of solid and liquid, if it is not

soft enough throughout to be easily broken up, if it has a pronounced disagreeable (putrid) odor, or if its color is obviously different from the agreed upon standard, the shipment shall be rejected without further test.

F-2. Sampling.— If the inspection (F-1) justifies sampling, and if the packages contain not more than 10 pounds of dry powder (Grade A and/or Grade B, Type 1) or not more than 1 gallon of paste (Grade B, Type 2), the inspector shall take another unopened container which he shall distinctly mark and send to the laboratory for test. While it is always desirable to send original containers for testing, with containers containing more than 10 pounds of powder or more than 1 gallon of paste, the inspector may thoroughly mix the contents of the sample inspected and transfer not less than one pound of the thoroughly mixed material to a clean glass container which it must nearly fill, close with a well fitting, clean dry stopper or lid and mark distinctly. He should take another sample to hold in case of dispute, and if so requested should take another sample for the seller. He must always furnish the laboratory with a complete copy of the manufacturer's directions for mixing and using, or specifically state that no such directions are furnished by the manufacturer.

F-3. Testing.—

F-3-a. Preliminary tests.— On opening the package note the condition of the contents (See F-1).

F-3-b. Mixing and working.— Place 100 g of ~~the sample~~ ^{powder paint or} in a 400-ml beaker and 100 ml of water (at 70°F) in a measuring cylinder. Gradually add a part of the water to the powder, stirring thoroughly until a heavy paste is obtained. Continue stirring and when all lumps are broken up add gradually more of the water until the mixture is of a creamy consistency. Allow to stand in this condition for 20 minutes, stirring occasionally so as to break up all lumps. Note the amount of water remaining in the graduate. The amount of water used with satisfactory Grade A and Grade B, Type 1 material will be about 85 to 100 ml, and with Grade B, Type 2 material 50 to 70 ml. Divide the well-mixed water paint into two approximately equal portions. When the manufacturer so advises, gradually add to one of these while stirring 5 ml of linseed oil. Apply each of these paints, by brushing, to white milk glass panels and also to wall board panels. Note ease of brushing. Let the panels dry and when so specified compare the color and smoothness and resistance to rubbing with similar panels made with the standard mutually agreed upon. If the paint is white, test its brightness by applying to milk glass a film of the paint without added linseed oil. Determine its brightness with a photometer \checkmark or by comparison

2. The Martens photometer using approximately diffuse reflection as described in B.S.Tech.Paper No.306 is satisfactory. This publication can be purchased for ten cents (not in

stamps from the Superintendent of Documents, Government Printing Office, Washington, D. C.

with a white matt surface the brightness of which is known and which is not less than 82 nor more than 86. Let the mixed paints stand at room temperature for 18 hours and then note the odor, and test with a paddle and by brushing to learn if the material is capable of ready remixing. (See note at the end of E-1-b.) Let the painted panels stand in a well-ventilated room for five days. Then make marks with a soft (No.2) lead pencil and wash with a sponge or soft rag that has been wet with soapy water at about 70°F and squeezed with the hand to remove excess water, and black cloth shall not be soiled by gentle rubbing on the dry paint film.

F-3-c. Casein (applicable to all grades and types).-

F-3-c-1. Qualitative tests.- Mix 15 to 20 g of the dry sample of cold water paint or 25 g of the paste with 50 ml of cold water. Let stand for about 30 minutes and then warm on a steambath. Filter and use the filtrate to determine the presence of casein or glue by the following tests:

Acree-Rosenheim formaldehyde reaction.- To 2 or 3 ml of the filtrate add 3 drops of formaldehyde solution (1 part 40% formaldehyde to 5000 parts water). Mix, and pour concentrated H_2SO_4 (containing a trace of iron) down the side of the tube; a purple ring indicates the presence of casein.

Millon's reaction.- To 5 ml of the original filtrate add a few drops of Millon's reagent (see Reagents), and heat to boiling. A white precipitate forms which slowly turns pink or red on heating. If in doubt, add a few more drops of the reagent and again boil. This reaction indicates casein.

Picric acid test for glue.- To 10 ml of the filtrate from the water-soluble portion of the cold water paint, add an equal volume of acid mercuric nitrate solution (see Reagents) and shake, add 20 ml of water and shake again. Let stand for five minutes, filter, and add an equal volume of saturated aqueous picric acid solution. If gelatine is present in large amounts, a yellow precipitate will immediately form; if only a very small amount, a cloudiness will be produced. A clear solution indicates that gelatine is absent. (Test will detect 1 part of gelatine in 10,000 parts of water.)

Confirmatory test for glue.- Filter the precipitate from the above procedure after shaking to produce coalescence. Wash with water containing two drops of concentrated ammonium hydroxide per 100 ml of water until the washings are slightly alkaline and then with water until the washings are neutral. Transfer the precipitate to a small beaker, add 10 ml of water and boil, filter and add twice

the volume of picric acid to the cool filtrate. The formation of a yellow precipitate indicates gelatine. (For a complete discussion of the picric acid procedure refer to Bogue^{3/}.)

3. R.H. Bogue, The Chemistry and Technology of Gelatine and Glue, p. 477. McGraw-Hill Book Co., New York City, 1922.

F-3-c-2. Quantitative method.- Transfer about 1 g (accurately weighed) of the sample into a 750-ml Kjeldahl flask. (In the case of Grade B, Type 2, weigh the paste in a small porcelain crucible or on a crucible lid, dry for two hours at 105 to 110°C and transfer the crucible or the lid and contents to the Kjeldahl flask.) Add 30 ml of concentrated sulphuric acid, 10 to 12 g of sodium sulphate and about 1 g of copper sulphate. Put a glass funnel in the mouth of the flask. Heat gently until the first vigorous frothing ceases, then raise the heat gradually until the liquid boils. Continue the boiling until the solution becomes practically colorless and clear except possibly with suspended siliceous material (three to four hours). Allow the flask to cool, dilute carefully with 150 ml of water, and again allow to cool. Place about 100 ml of 50 per cent sodium hydroxide solution in a measuring cylinder and gradually add small portions to the flask, gently swirling the flask (held underneath a stream of cold water) after each addition until about 40 to 45 ml of the hydroxide solution has been added. Then add the remainder of the hydroxide solution, pouring it carefully and slowly down the side of the flask held under the stream of cold water, so that it does not mix immediately with the acid solution. Add about 1 g of granulated zinc to prevent bumping and a piece of paraffin the size of a pea to diminish frothing. Connect the flask quickly with a condenser, the delivery tube of which dips into a 500-ml Erlenmeyer flask containing 50 ml of standardized (about 0.1 N) sulphuric acid diluted to about 100 ml. Carefully swirl the Kjeldahl flask to mix the contents and start to heat gently, increase the flame as the danger of foaming over diminishes, and finally boil briskly until about one-half of the liquid has passed over into the receiver. Disconnect the receiver, add methyl red solution (four drops) and titrate the excess acid with standardized (about 0.1 N) sodium hydroxide solution. A blank determination should be made using the reagents, digesting and distilling as with the sample.

F-3-c-3. Computation.- Subtract the volume of standardized NaOH solution used on the sample from the volume of standardized NaOH solution used on the blank and compute from the remainder the weight of casein, using the factor $0.014 \times 7.7 = 0.1078$ g casein per ml of normal NaOH. Then from the weight of the sample taken compute the percentage, or let

A = ml of NaOH solution used in blank

B = ml of NaOH solution used with sample

W = weight of sample in g

Then $\frac{100 (A - B) \times \text{normality of NaOH soln.} \times 0.1078}{W}$ = per cent casein

F-3-d. Free lime as Ca(OH)_2 (applicable to Grade A only).— Weigh accurately 2 g of the sample into a 500-ml graduated flask, add 40 g of sugar (sucrose) and 200 ml of water and shake vigorously every 15 minutes for two hours; dilute to the mark with water, mix, and allow to settle (about one hour). Measure accurately 250 ml (equivalent to 1 g of the sample) of the practically clear solution and titrate with standard (approximately 0.1 N) hydrochloric acid, using phenolphthalein indicator. One ml of 0.1 N HCl is equivalent to 0.0037 g of Ca(OH)_2 .

F-3-e. Sum of ZnS and TiO_2 (applicable to Grade B, Types 1 and 2 only).— Make qualitative tests using regular methods of qualitative analysis to determine whether the material contains ZnS or TiO_2 or a mixture of these. It is also advisable to make a qualitative test for phosphates, since an appreciable amount of phosphate will necessitate modification of the method for determining TiO_2 .

Weigh accurately about 1 g of the sample, transfer to a 400-ml beaker, add 30 ml of hydrochloric acid (1:2), boil for two to three minutes, add 200 ml of water and a small piece of litmus paper; add strong ammonia until slightly

4. When interfering substances such as compounds of iron are present, filter at this point, add a slight excess of bromine water and 2 g of ammonium chloride, heat nearly to boiling, add an excess of ammonia, heat for about two minutes, filter, wash, and set aside the filtrate; wash the precipitate with dilute hydrochloric acid and ammonium chloride, add an excess of ammonia to the acid liquid passing through the paper, boil, filter, add to the original filtrate, evaporate to about 200 to 250 ml and titrate with ferrocyanide.

alkaline, render just acid with hydrochloric acid, then add 3 ml of strong hydrochloric acid, heat nearly to boiling and titrate with standard ferrocyanide as in standardizing that solution (See F-4-b). When (as is generally the case) the material contains only inappreciable amounts of zinc in any form other than ZnS , the total zinc can be computed as ZnS (ZnO factor for ferrocyanide solution $\times 1.2 = \text{ZnS}$, or Zn factor $\times 1.49 = \text{ZnS}$). When other compounds of zinc are present in appreciable amounts, take another accurately weighed portion of about 1 g, add 100 ml of 1 to 3 per cent acetic acid, stir vigorously, but do not heat, cover and let stand for 18 hours, stirring once every five minutes for the first half hour. Filter, wash with dilute acetic

acid and titrate the zinc in the clear filtrate. Compute as ZnS and subtract from the total zinc as ZnS determined above.

When titanium oxide is present, weigh accurately about 1 g of the sample in a porcelain crucible, heat gently to drive off water, and finally ignite slowly and at a low heat until organic matter is destroyed. Cool and brush the contents of the crucible into a 250-ml Pyrex beaker. Carefully crush any lumps with a rounded glass rod, add 25 ml of concentrated sulphuric acid and 3 g of ammonium sulphate. Mix well and heat on a hot plate until fumes of sulphuric acid are evolved, and then continue the heating over a strong flame until solution is complete (usually not over five minutes of boiling) or it is apparent that the residue is composed of silica or siliceous matter. Caution should be observed in handling this hot acid solution. Cool the solution, dilute with 100 ml of water, stir, heat carefully to boiling while stirring, settle, filter through paper and transfer the precipitate completely to the paper. Wash the insoluble residue with cold 5 per cent (by volume) sulphuric acid until all titanium is removed.

Dilute the filtrate to 200 ml and add about 30 ml of ammonium hydroxide (specific gravity 0.90) to lower the acidity to approximately 5 per cent sulphuric acid (by volume).

Wash out a Jones reductor ⁵ with dilute 5 per cent (by volume) sulphuric acid and water, leaving sufficient

5. Directions for preparing a Jones reductor may be found in "Applied Inorganic Analysis", Hillebrand and Lundell, J. Wiley and Sons, New York City, p.100, or Treadwell-Hall, Analytical Chemistry, 5th Ed., J. Wiley and Sons, p.368.

water in the reductor to fill to the upper level of the zinc. (These washings (200 to 300 ml) should require not more than one or two drops of 0.1 N potassium permanganate solution to obtain the pink color.) Empty the receiver, and put in it 25 ml (measured in a graduate) of ferric sulphate solution. (See F-4-d.) Reduce the prepared titanium solution as follows: (1) Run 50 ml of the 5 per cent sulphuric acid solution through the reductor at a speed of about 100 ml per minute, (2) follow this with the titanium solution, (3) wash out with 100 ml of 5 per cent sulphuric acid, (4) finally run through about 100 ml of water.

Care should be observed that the reductor is always filled with solution or water to the upper level of the zinc.

Gradually release the suction, wash thoroughly the glass tube that was immersed in the ferric sulphate solution, remove the receiver, add 5 ml of syrupy phosphoric acid, reagent quality, and titrate immediately with 0.1 N potassium permanganate solution. (See F-4-c.)

1 ml 0.1 N KMnO_4 = 0.0048 g Ti = 0.0080 g TiO_2

Run a blank determination, using the same reagents, washing the reductor as in the above determination. Subtract this permanganate reading from the original reading and calculate the final reading to titanium dioxide (TiO_2) (which will include iron, chromium, and any other substance which is reduced by zinc and acid.) With white paints interfering substances are probably absent. With tinted paints iron is likely to be present. If it is, determine total iron as Fe_2O_3 by any suitable method, multiply by 1.003 and subtract this figure from the TiO_2 as determined above and report the remainder as TiO_2 .

F-4. Reagents.-

F-4-a. Uranyl indicator.- 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.

F-4-b. Standard potassium ferrocyanide.- Dissolve 22 g of the pure salt in water and dilute to 1000 ml. To standardize, transfer about 0.2 g (accurately weighed) of pure metallic zinc or freshly ignited pure zinc oxide to a 400-ml beaker. Dissolve in 10 ml of hydrochloric acid and 20 ml of water. Drop in a small piece of litmus paper, add ammonium hydroxide until slightly alkaline, then add hydrochloric acid until just acid, and finally 3 ml of strong hydrochloric acid. Dilute to about 250 ml 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 one minute. A blank should be run with the same amounts of reagents and water as in the standardization and in titration of the sample. The standardization must be under the same conditions of temperature, volume, and acidity as existing when the sample is titrated.

F-4-c. 0.1 N potassium permanganate solution.- Dissolve 3.161 g of pure potassium permanganate in a liter of distilled water, let stand 8 to 14 days, siphon off the clear solution (or filter through an asbestos filter), and standardize as follows: In a 400-ml beaker dissolve 0.25 to 0.30 g of Bureau of Standards sodium oxalate in 250 ml of hot water (80 to 90°C) and add 15 ml of dilute sulphuric acid (1:1). Titrate at once with the potassium permanganate solution, stirring the liquid vigorously and continuously. The permanganate must not be added more rapidly than 10 to 15 ml per minute, and the last 0.5 to 1 ml must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The solution should not be below 60°C by the time the end point is reached. (More rapid cooling may be prevented by allowing the beaker to stand on a small asbestos covered hot plate during the titration. The use of a small thermometer as a stirring

rod is most convenient.) The weight of sodium oxalate used multiplied by 0.8334 gives its iron equivalent, or multiplied by 1.1954 gives its titanium dioxide (TiO₂) equivalent.

The permanganate solution should be kept in a glass-stoppered bottle painted black to keep out light.

F-4-d. Ferric sulphate solution.- Dissolve 180 g of pure ferric ammonium sulphate (FeNH₄(SO₄)₂ + 12 H₂O, meeting the specifications of the American Chemical Society, in 600 ml of distilled water, add 80 ml of strong sulphuric acid, mix, and dilute to one liter. Twenty-five ml of this solution should require not over one or two drops of decinormal potassium permanganate for a "blank". Occasionally solutions thus prepared have shown an objectionable purple or violet color. In this case the material should be rejected, and a new lot obtained or the solution may be prepared from ingot iron (for example Bureau of Standards Standard Sample No. 55a) dissolving 20 g of the ingot iron in a liter beaker with 450 ml of dilute sulphuric acid (80 ml of strong sulphuric acid, sp.gr. 1.84, plus 370 ml of water). Place on a hot plate, and keep just below boiling for about one hour. Filter off the carbon, cool, oxidize with strong hydrogen peroxide (30 per cent by volume), boil off excess peroxide, and dilute to one liter.

F-4-e. Tenth normal standard sodium hydroxide solution.-

Prepare a stock concentrated solution of sodium hydroxide by dissolving hydroxide in water in the proportion of 200 g of NaOH to 200 ml of water. Allow this solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the precipitate of sodium carbonate into another clean bottle. Add clear barium hydroxide solution until no further precipitate forms. Again allow to settle until clear. Draw off about 70 ml and dilute to 10 liters with freshly boiled distilled water. Preserve in a stock bottle provided with a large guard tube filled with soda lime. This solution will be approximately one-tenth normal, but do not attempt to adjust it to any exact value. Determine its exact strength and make proper corrections in using it. Determine its exact strength by standardizing against pure acid potassium phthalate (HKC₈H₄O₄), Bureau of Standards Standard Sample No. 84, as follows: Accurately weigh about 1 g of the dried acid potassium phthalate and transfer to a 300-ml flask which has been swept free from carbon dioxide. Add 50 ml of cool water that is free from carbon dioxide, stopper the flask and shake gently until the phthalate is dissolved. When the sample is in solution, add 3 drops of a 1 per cent solution of phenolphthalein and titrate with the above-mentioned, approximately 0.1 N solution of sodium hydroxide. Determine the quantity of sodium hydroxide required to produce the end point by matching the color

in another flask containing the indicator and the same volume of water free from carbon dioxide. Subtract the amount required from that used in the first titration and calculate the normality of the alkali solution on the basis of the following equation: 1.0207 g of acid potassium phthalate is equivalent to 50 ml of 0.1 N solution of sodium hydroxide.

$$\text{Normality of NaOH} = \frac{\text{weight of HKC}_8\text{H}_4\text{O}_4 \times 4.89803}{\text{ml NaOH}}$$

F-4-f. Tenth normal sulphuric acid solution.- Add about 3 ml of sulphuric acid (1.84 specific gravity) to the distilled water, cool and dilute to 1000 ml. Determine the exact strength by titrating against freshly standardized sodium hydroxide or by any other accurate method. Either adjust to exactly tenth normal strength or leave as originally made and make proper corrections in using it.

F-4-g. Mercuric nitrate solution.- Dissolve 5 g of mercury in 10 ml of concentrated HNO_3 (sp.gr. 1.42) and to this solution add 25 times its volume of water. (This solution should give no turbidity with the picric acid solution.)

F-4-h. Millon's Reagent.- Dissolve 1 part by weight of mercury in 2 parts of concentrated nitric acid and dilute with twice its bulk of water, allow the precipitate to settle and use the supernatant liquid. (Detects the tyrosine group in proteins - H_2O_2 , alcohol, and chloride interfere.)

F-4-i. Standard hydrochloric acid solution (approximately 0.1 N).- About 8.5 ml of concentrated HCl , sp.gr. 1.18 per liter. The solution may be standardized against the standard NaOH solution (see F-4-e) or by any other accurate method.