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RECOMMENDED SPECIFICATION FOR CERAMIC WHITING.

This is the fifth of a series of specifications for the lime used in various chemical industries. To assist in the development of these specifications, the bureau has called together an Interdepartmental Conference on Chemical Lime, composed of representatives of the Geological Survey and Bureau of Mines of the Interior Department; the Bureau of Soils, Bureau of Chemistry, Forest Service, and Fixed Nitrogen Research Laboratory of the Department of Agriculture; and the Chemical Warfare Service of the War Department. The present specification, based on a draft originally prepared by A. E. Williams, of the ceramics division, Bureau of Standards, has been unanimously approved by the above conference and by the whiteware division of the American Ceramic Society.

ABSTRACT.

Ceramic whitening is a finely divided form of calcium carbonate (marble) used as a flux in the manufacture of ceramics. It should be of about 97 per cent purity, and 98 per cent should pass a No. 200 screen.

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I. GENERAL.

1. DEFINITION OF CERAMIC WHITING.—Ceramic whiting is a finely ground white powder composed of nearly pure calcium carbonate or calcium carbonate and magnesium carbonate obtained from pulverizing and sizing chalk, marble, or limestone, or as a chemically precipitated product.

2. USE OF WHITING IN CERAMIC PRODUCTS.—Whiting is used to furnish the calcium oxide component of glazes, enamels, and fluxed ceramic bodies. It is an active fluxing agent, rarely used in large quantities in body mixtures. It may be used either as a raw ingredient in glazes or fritted or smelted with other glaze materials before application.

3. PACKING.—Whiting is packed and shipped in barrels holding not more than 325 pounds or bags holding not more than 125 pounds. The package should be labeled, stating whether the contents is a natural rock whiting or a chemically precipitated whiting.

II. REQUIREMENTS.

1. QUALITY.—Whiting shall be uniform in quality (from shipment to shipment), both as to fineness of grain and composition. The calcium, magnesium, or total carbonates shall not vary more than 1 per cent and the silica not more than one-half of 1 per cent from a figure set by contract within the limits of the composition shown in class 1 or class 2. It should be manufactured from the purest rock available and should be practically free from particles of pyrites, iron-bearing silicates, metallic iron, and gypsum.

2. COMPOSITION.—Whitings shall be divided into two classes, No. 1 being practically a pure calcium carbonate and No. 2 containing calcium carbonate, with a considerable percentage of magnesium carbonate within the limits of the composition given. This does not indicate that one class is inferior in quality to the other, but indicates that numerous users prefer the magnesium whiting to the pure calcium whiting.

TABLE 1.—Composition.

| Constituents. | Class 1. | | Class 2. | |
|---|---------------|---------------|---------------|---------------|
| | Maxi- mum. | Mini- mum. | Maxi- mum. | Mini- mum. |
| Total carbonates..... | Per cent. | Per cent. | Per cent. | Per cent. |
| CaCO ₃ | | 97 | | 97 |
| MgCO ₃ | 2 | 96 | 8 | 89 |
| Fe ₂ O ₃ | .25 | | .25 | |
| SiO ₂ | 2 | | 2 | |
| Total S computed to SO ₃ | .1 | | .1 | |

3. **FINENESS.**—Screening samples by washing for 10 minutes with stream of water practically without pressure shall not leave a residue of more than 1 per cent on a No. 140 screen (or more than 2 per cent on a No. 200 screen), and at least 98 per cent of the material shall pass a No. 200 screen. It shall also be so fine that a separation made by a Pearson¹ air separator will show at least 85 per cent of the material finer than 0.02 mm and at least 48 per cent finer than 0.01 mm.

As an alternative to the Pearson air-separator method the following (not so desirable) may be used: 2½ g of the material shall be shaken for 10 minutes in a 250 cc cylindrical graduate with 250 cc of distilled water. On allowing to settle it shall require not less than 20 minutes for visible settling to cease when the cylinder is viewed in reflected light, using clear, north-sky light for illumination.

4. **MARKING.**—Each shipment of material shall be legibly marked with the names of consignor and consignee and with some means of identifying the particular contract on which the shipment is made.

5. **RETESTING.**—Notice of the rejection of a shipment based on these specifications must be in the hands of the consignor within 10 days after the receipt of the shipment at the point of destination. If the consignor desires a retest, he shall notify the consignee within five days of receipt of said notice.

III. SAMPLING AND TESTING.

1. **SAMPLING.**—Twenty-five per cent of the number of packages shall be selected for sampling. A core representing the contents of each of these packages shall be taken with a sampling tube. The total material so collected shall weigh not less than 5 pounds. This shall be thoroughly mixed and quartered to provide a half-pound sample for the laboratory.

2. **TESTING.**—The following directions for analytical work are adapted from American Society for Testing Materials tentative methods of chemical analysis of limestone, quicklime, and hydrated lime, C25-22T. For further information on this subject, reference should be made to "The analysis of silicate and carbonate rocks," by W. F. Hillebrand, U. S. Geological Survey, Bulletin No. 700.

¹ The Pearson air separator, developed at the Bureau of Standards by J. C. Pearson and F. A. Hitchcock, gives excellent separations of fine, dry powders and is the only machine which can be used for this purpose for particles as small as 0.01 mm. Its use is, therefore, recommended for manufacturers and users of fine powder, such as whiting, flint, feldspar, paint pigments, etc.

Weigh out 0.5 g of the substance and ignite in a covered platinum crucible in an electric muffle (or over a blast lamp, if no muffle is available) for 15 minutes, or longer if the heat is not powerful enough to effect complete decomposition within that time. Transfer to an evaporating dish of platinum or porcelain, but not of glass, mix to a thin slurry with distilled water, add 5 to 10 cc of HCl (sp. gr. 1.20) and digest with aid of gentle heat and agitation until solution is complete. Solution may be aided and the time shortened by light pressure with the flattened end of a glass rod upon resistant lumps. Then evaporate the solution to dryness, so far as this may be possible on the water bath.

When dry or nearly so, place the dish and its contents in an air bath or (covered) on a platinum triangle resting on a hot plate and heat for one hour at 200° C. Drench the cooled mass with HCl (sp. gr. 1.20) and allow to stand for a few minutes. Add an equal volume of water, cover the dish and digest on the water bath for 10 minutes. Separate the silica by filtration on a filter of suitable size. Wash thoroughly with dilute HCl and then wash twice with cold water.

Evaporate the filtrate to dryness. Digest the residue with HCl and water, as before, but allowing only a few minutes time. Filter this solution through a second and smaller paper.

Transfer, wet, the papers containing the separated residues to a weighed platinum crucible. Char carefully without allowing the paper to inflame and ignite to constant weight and weigh. Correct the weighed silica for foreign matter by evaporating with 5 cc of HF and one or two drops of H₂SO₄. Heat the residue for two or three minutes in an electric muffle and again weigh. The difference between this weight and that previously obtained gives the weight of the silica.

Fuse the residue from the silica determination using a little Na₂CO₃. Dissolve the cooled melt in HCl and add the solution to the filtrate from the second evaporation for silica. Add a few drops of bromine water or HNO₃ and boil the solution until all trace of bromine or chlorine is gone. Then add HCl, if not already present, sufficient to insure a total volume of 10 to 15 cc of HCl (sp. gr. 1.20). Add a few drops of methyl red solution and after diluting to 200 to 250 cc heat the liquid to boiling. Neutralize by means of NH₄OH (dilute toward the end) until the color of the liquid changes to a distinct yellow. Boil for one or two minutes, allow to settle, filter, and wash the precipitate at once

two or three times with hot NH_4Cl (2 per cent) solution and suck dry.

Set the filtrate aside. Dissolve any precipitate from the paper in hot, dilute HCl , the solution passing into the beaker in which the precipitation was made, and wash the paper thoroughly with hot water. Boil the solution to expel any trace of chlorine and again precipitate the hydroxides with NH_4OH as described above. Ignite the precipitate, moist, in a weighed platinum crucible, cool, and weigh as Al_2O_3 and Fe_2O_3 .

Add a few drops of NH_4OH to the combined filtrate from the R_2O_3 precipitate and bring the solution to boiling. To the boiling solution add 35 cc of a saturated solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and continue the boiling until the precipitated CaC_2O_4 assumes a granular form; then allow it to stand at least one hour, or until the precipitate has settled and the supernatant liquid is clear, filter and wash three or four times with boiling water. Place the wet filter and precipitate in a platinum crucible and burn off the paper over the small flame of a Bunsen burner, or in a muffle. Ignite the residue, dissolve in hot dilute HCl , and make up the volume of the solution to 100 cc with water. Add NH_4OH in slight excess and boil the liquid. If a small amount of $\text{Al}_2(\text{OH})_6$ separates, filter it out, wash with NH_4Cl (2 per cent solution), ignite, weigh and add this weight to that found in the first determination. Then reprecipitate the lime by $(\text{NH}_4)_2\text{C}_2\text{O}_4$, allow to stand until settled, filter, wash three or four times with boiling water, and weigh as calcium oxide after ignition to constant weight in a covered platinum crucible.

Acidify the combined filtrates from the calcium precipitates with HCl and concentrate on the water bath to about 150 cc and heat to boiling. To the boiling solution add 10 cc of a saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ and continue the boiling for several minutes. Then cool to room temperature and add NH_4OH drop by drop with constant stirring until the crystalline ammonium-magnesium orthophosphate begins to form and then in moderate excess, the stirring being continued for several minutes. Allow the liquid to stand in a cool atmosphere for from 12 to 48 hours and filter.

Dissolve the precipitate in hot dilute HCl , make up the solution with water to about 100 cc, add 1 cc of the saturated solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$ and NH_4OH drop by drop with constant stirring until the precipitate is again formed as above described and the

ammonia is present in moderate excess. Then allow it to stand in a cool atmosphere for from 12 to 48 hours, filter on paper or a Gooch crucible, wash with dilute NH_4OH containing NH_4NO_3 , ignite, cool, and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$.

Dissolve 2 to 5 g (depending upon the amount of iron present) of the properly prepared sample in HCl and evaporate rapidly to dryness. Treat the residue with water and HCl , filter off the silica, and wash several times with hot water. Precipitate the iron in a boiling solution with ammonium hydroxide, allow to settle, filter, and wash free of chlorides, using hot water. Dissolve in dilute H_2SO_4 .

Ignite the insoluble matter from the evaporated hydrochloric acid solution in a platinum crucible. Treat with H_2SO_4 and HF and heat until fumes of H_2SO_4 appear. Bring the residue into solution with the addition of a few drops more of H_2SO_4 and combine the solution with that of the bulk of the iron. Reduce this solution by zinc and titrate the iron with KMnO_4 in the usual manner.

Carbon dioxide is to be determined upon the properly prepared sample according to the method given in U. S. Geological Survey Bulletin No. 700, page 217. An illustration showing the arrangement of the component parts of the necessary apparatus is shown on page 218 of that bulletin.

Boil a 0.5 g sample with dilute HCl in a small Erlenmeyer flask attached to an upwardly inclined condenser, whence, after passing through a drying system—calcium chloride, anhydrous copper sulphate to retain hydrogen sulphide from decomposable sulphides and any HCl that may pass over, then calcium chloride again—the carbon dioxide is caught by absorption tubes filled with soda lime followed by calcium chloride. Of course, arrangement is made for a current of air free from CO_2 with which to sweep out the apparatus before and after the experiment and for a slow current during its continuance.

The manipulations are as follows: Pour hot water upon the powder in the flask fitted with a separatory funnel and delivery tube; attach this to the condenser and force a current of air free from CO_2 through the whole system, except the weighed absorption tubes, until the original air has been displaced, the observation bulbs (containing H_2SO_4 to show the rate of gas flow) being attached directly to the drying system. Then close the stopcock in the separatory funnel, half fill the latter with HCl (1:1), re-

place the rubber stopper of the funnel, insert the absorption tubes between the drying system and the observation bulbs, and allow the acid to flow into the flask, slowly if there is much carbon dioxide, rapidly if there is but little. When effervescence diminishes in the former case, at once in the latter, light the burner under the flask and start the flow of water through the condenser. Keep the flame low, so as to secure steady but quiet ebullition, and do not interrupt the air current although it should be reduced to a slow rate. With much carbon dioxide the rate of absorption is very readily noted by holding the hand to the soda-lime tubes, which become hot or warm when absorption is taking place. Sufficient time having elapsed, extinguish the flame and increase the air current. When cool, disconnect the soda-lime tubes from the apparatus and allow to stand in the balance case until two weights taken 30 minutes apart agree within 0.5 mg.

The soda lime for use in this determination must be porous, not hard and unabsorptive like that sometimes used for the combustion of nitrogenous organic substances.

Digest 2 g of the properly prepared sample on the hot plate with 25 to 30 cc of bromine water. Then add 15 cc of dilute HCl (1:1) and boil until all bromine has been expelled. Filter through a small paper and wash the residue thoroughly with hot water. Dilute the filtrate to 250 cc, heat to boiling, and add 10 cc of a boiling 10 per cent solution of barium chloride, drop by drop, with constant stirring. Stir well and allow to stand overnight. Filter, wash with boiling water, ignite, and weigh as BaSO_4 .

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