DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS.
GEORGE K. BURGESS, Director.

CIRCULAR OF THE BUREAU OF STANDARDS.

No. 144.

[JULY 6, 1923.]

RECOMMENDED SPECIFICATION FOR LIMESTONE AND QUICKLIME FOR USE IN THE MANUFACTURE OF SULPHITE PULP.

ABSTRACT.

Limestone or quicklime is used to prepare the cooking liquor in which wood is cooked to reduce it to paper pulp. It is customary to use a high calcium limestone when preparing liquor by the tower process or a high magnesian quicklime with the tank process, but other kinds of limestone or quicklime are being used. The specifications, therefore, cover high calcium and high magnesium limestone and quicklime on a basis of about 95 per cent purity.

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This is the fourth 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 F. A. Curtis, of the paper section, Bureau of Standards, has been unanimously approved by the above conference, by the National Lime Association, and by the Technical Association of the Pulp and Paper Industry

I. GENERAL.

1. MANUFACTURE OF SULPHITE PULP.

(*a*) Outline of Process.—The manufacture of pulp for paper making from wood by means of the sulphite process consists of the following operations: (1) Preparation of the wood, (2) preparation of the cooking liquor, (3) cooking of the wood, (4) washing and screening the pulp, (5) bleaching the pulp, and (6) preparation of the finished pulp for shipment.

The use of limestone and lime in this manufacturing process occurs in the preparation of the cooking liquor. This liquor is produced by the reaction between sulphur dioxide and limestone or lime, and the two absorption methods in common use are called the tower system and the tank system. The liquor is essentially a calcium or calcium and magnesium salt of sulphurous acid, and its function is to affect the noncellulose part of the wood in such a manner that, in the washing and bleaching process, nearly pure cellulose may be obtained.

(*b*) Kind of Stone and Lime required.—There is some difference of opinion in this country as to the relative merits of high calcium and high magnesium stone and lime for use in the two absorption systems. The difference in practice in the various pulp mills does not seem to be based on accurate data.

2. LIMESTONE.

(*a*) Definition.—Limestone consists, essentially, of calcium carbonate or of calcium and magnesium carbonate, where the amount of the latter does not exceed 45.5 per cent.

(*b*) USE OF LIMESTONE IN THE TOWER SYSTEM.—The tower type of absorption system consists of one or more towers varying in height from 20 to 150 feet and charged with limestone resting on gratings. A stream of water, with or without the addition of reclaimed liquor, trickles over this stone, while the sulphur dioxide enters at the bottom, rises, and acts upon the moist stone and is absorbed by the downward flowing film of water.

(*c*) KIND OF STONE PREFERRED.—In the tower system high calcium stone is desired, due principally to the fact that when high magnesium stone is used the calcium carbonate goes into solution first, causing the stone to crumble and leave a sludge. For this reason, in a tower system using high magnesium stone, it is customary to have the grates raised 40 to 50 feet, and they require frequent cleaning. One mill is using and recommends high magnesium stone. However, most of the mills are using high calcium stone, and, in fact, several are using marble having a calcium carbonate content of 98.5 per cent. It can not be said, however, that high magnesium stone can not be used in the tower system, but it is not the most common practice.

(*d*) PACKING.—Limestone is shipped in bulk in carload lots.

3. QUICKLIME.

(*a*) DEFINITION.—Quicklime is the product resulting from the calcination of limestone and consists, essentially, of calcium oxide or of calcium and magnesium oxides. It will slake when water is added to it, and this slaking is accompanied by an evolution of heat and an increase in volume.

(*b*) USE OF LIME IN THE TANK SYSTEM.—In the tank or milk of lime system the lime is in solution or suspension in a series of tanks, equipped with suitable agitators. The sulphur dioxide is forced or drawn through these tanks successively. The contents of the first tank are drawn off when the liquor has reached a certain strength (3.5 to 6 per cent total SO_2), and the contents of the second and third tanks progress to the first and second tanks, respectively. The third tank is again charged with fresh milk of lime. In some cases the tanks are built on top of each other in the form of a tower, and the process may then be operated continuously.

(*c*) KIND OF LIME PREFERRED.—In the tank system a lime high in magnesium is desired, due to the fact that the magnesium salts are soluble, while the calcium salts are not so soluble and have a tendency to clog the system. But, due to variations in tank

systems, it is probable that a high calcium lime would give good results in certain instances.

(*d*) PACKING.—Quicklime is shipped either in bulk, in carload lots, or barrels holding 180 pounds net or 280 pounds net each.

II. REQUIREMENTS.

1. QUALITY.

The quality of the stone or lime should be reasonably uniform, and in the case of the high magnesium stone or lime the proportions of magnesium and calcium should be kept as nearly constant as possible.

2. LIMESTONE.

(*a*) COMPOSITION.—In view of the fact that various systems may use different grades of stone or lime, the requirements of these specifications are so given that they will meet the conditions of the pulp mills in this country. The maximum and minimum quantities are given in the following table:

TABLE 1.—Composition of Limestone.

Ingredients.	High calcium stone.		High magnesium stone.	
	Maximum.	Minimum.	Maximum.	Minimum.
Calcium oxide	.....	53.0	.....	29.8
Magnesium oxide	1.5	.....	.....	17.9
Oxides of silicon, iron, and aluminum	1.5	.....	1.5	.....
Organic matter	.5	.....	.5	.....

(*b*) IMPURITIES.—The impurities present in a limestone must be evenly distributed throughout the mass and must not be concentrated in visible strata or nodules which would clog the grates. The stone shall contain no strata of an argillaceous or organic nature which might cause the pieces of limestone to split.

(*c*) SIZE.—Each piece of limestone shall be large enough so that it will be retained on a 3-inch ring, but small enough so that it can be lifted readily by one man.

(*d*) DENSITY.—Limestone shall be of such a density that a block of it will weigh not more than 180 nor less than 150 pounds per cubic foot.

3. QUICKLIME.[1]

TABLE 2.—Composition of Quicklime.

Ingredients.	High calcium lime.		High magnesium lime.	
	Maximum.	Minimum.	Maximum.	Minimum.
Calcium oxide	.....	92.5	.....	55.4
Magnesium oxide	2.5	.....	.....	39.6
Oxides of silicon, iron, and aluminum	3.0	.....	3.0	.....

4. MARKING.

Each carload of material or fraction thereof shall be legibly marked with the names of the 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 the notice of rejection. The consignee shall provide all reasonable facilities to permit the consignor to resample the material. This retest shall be at the expense of the consignor.

III. SAMPLING AND TESTING.

1. SAMPLING.

The purchaser will bear all expense of sampling and testing. When limestone or quicklime is shipped in bulk, the sample shall be so taken that it will represent an average of all parts of the shipment from top to bottom and shall not contain disproportionate share of the top and bottom layers. The sample shall consist of 1 shovelful for each 3 tons of material, but not less than 10 shovelfuls taken from different parts of the shipment. The total sample

[1] The above requirements as to the composition of quicklime are based on the sample as received. If it is desired to use the nonvolatile basis, the figures should be changed to the following:

Composition of quicklime on nonvolatile basis.

Ingredients.	High calcium lime.		High magnesium lime.	
	Maximum.	Minimum.	Maximum.	Minimum.
Calcium oxide	.....	94.3	.....	56.5
Magnesium oxide	2.6	.....	.....	40.4
Osides of silicon, iron, and aluminum	3.1	.....	3.1	.....
Carbon dioxide	5.0	.....	5.0	.....

taken shall weigh at least 100 pounds and shall be crushed to pass a 1-inch ring; mixed thoroughly, and "quartered" to provide a 15-pound sample. This 15-pound sample shall be crushed to pass a one-half inch ring, mixed thoroughly, and quartered to provide a 2-pound sample for the laboratory. In case a shipment consists of more than 1 car, a separate sample shall be taken from each car.

When quicklime is shipped in barrels, at least 3 per cent of the number of barrels shall be sampled. They shall be taken from various parts of the shipment, dumped, mixed, and sampled as specified in the above paragraph.

When sampling quicklime, it is essential that the operation be conducted as expeditiously as possible in order to avoid undue exposure of the material to the air. The sample to be sent to the laboratory shall immediately be placed in an air-tight container in which the unused portion shall be stored until the shipment has been finally accepted or rejected by the purchaser.

2. TESTING.

The following directions are a brief summary of the analytical methods which are recommended. For more complete information on this subject references should be made to The Analysis of Silicate and Carbonate Rocks, by W. F. Hillebrand, U. S. Geological Survey, Bulletin No. 700.

Blast 0.5 g of the sample for 15 minutes in a platinum crucible. Cool and transfer to an evaporating dish. Mix to a slurry with distilled water. Add 5 to 10 cc concentrated HCl. Heat gently until solution is complete, breaking up lumps if necessary. Evaporate to dryness on water bath. Add 5 to 10 cc concentrated HCl, and dilute with an equal volume of distilled water. Digest on water bath for 10 minutes. Filter and wash with hot water. Evaporate the filtrate to dryness. Dissolve in acid and water as before. Filter and wash with hot water. Ignite the two precipitates together and weigh as silica and insoluble matter.

Dilute the above filtrate to 250 cc. Add HCl, if necessary, to insure a total volume of 10 to 15 cc of this acid in this solution. Make alkaline with NH_4OH. Boil until odor of NH_3 is barely noticeable. Filter and wash slightly with hot water. Dissolve the precipitate with hot dilute HCl and repeat the precipitation as before. Filter and wash thoroughly with hot water. Ignite and weigh as oxides of iron and aluminum.

To the filtrates from the above add a few drops of NH_4OH and bring to a boil. Add 25 cc of a saturated solution of $(NH_4)_2C_2O_4$. Continue boiling until the precipitate becomes granular. Let stand until precipitate settles clear. Filter and wash with boiling water. Ignite the precipitate, dissolve in dilute HCl, and dilute to 100 cc. Add excess of NH_4OH and boil. Filter out any insoluble matter, ignite and weigh, and add its weight to the oxides of iron and alumina found previously. To this filtrate add $(NH_4)_2C_2O_4$, proceeding as before. Filter and wash with boiling water. Ignite and blast to constant weight as calcium oxide.

Acidify the filtrates from the above with HCl. Evaporate to 150 cc. Add 10 cc of a saturated solution of $NaNH_4HPO_4$. Add NH_4OH drop by drop, with constant stirring, until the precipitate starts to form. Then add moderate excess of NH_4OH. Stir for several minutes. Let stand over night. Filter and dissolve the precipitate in hot dilute HCl. Dilute to 10 cc, add 1 cc of saturated solution of $NaNH_4HPO_4$, and precipitate as before. Filter and wash with an alkaline solution made by diluting NH_4OH until it contains about 2½ per cent NH_3 and then add a few drops of HNO_3. Ignite and weigh as $Mg_2P_2O_7$. Multiply this weight by 0.3621 to find the weight of MgO.

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