Figure 7. Plow on injection rig

from the tanks terminate at the base of three plows, which in operation allow the ammonia and acid to be placed 6 to 9 inches below the surface of the ground (Figure 7). The ammonia outlet precedes the acid outlet. A metering pump consisting of a rotating reel which presses against a number of plastic hoses is used to maintain a uniform flow of acid to each plow. In the operation of injection rigs the presence of solids in wet-process acid is less critical, for the acid is moved by a nonclogging, positive displacement pump, and the flow of acid can be constantly supervised by the operator of the rig.

Both electric furnace acid and wet-process acid are used in the above ap-

plications. The bulk of the acid applied is electric furnace acid, but for economic reasons as the quality of wet-process acid is improved, its use in irrigated areas is certain to increase.

Acknowledgment

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FERTILIZER MICROSTRUCTURE

Preparation of Thin Sections of Triple Superphosphate for Microscopic Examination

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DURING a study of the physical properties of triple superphosphate, a method was needed for microscopic comparison of samples with respect to crystal growth, porosity, and general structure of the particle. The usual method of preparing and examining thin sections of a sample seemed attractive because it allows a minute study of the internal structure of the particle. Methods for preparing thin sections of hard, brittle materials, such as geological specimens, for microscopic examination

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are well documented in the technical literature (1–3, 5).

Techniques and types of materials used in the procedure vary with the type of sample being examined. The soft, porous, water-soluble properties of triple superphosphate cause it to require special consideration when making it into thin sections, in order to avoid smearing and other distortion of the grain structure during grinding and polishing of the specimen. Common procedures applicable to geological specimens needed modification when applied to triple superphosphate. For example, the

method of Reed and Mergner (6) for impregnating limestone samples with Canada balsam dissolved in xylene is not satisfactory for superphosphate because of the difficulty in evaporating the xylene from the pores and interstices of the particle. The present paper describes a technique which was developed for encapsulating and impregnating triple superphosphate with a thermosetting polyester-type resin which could be sawed, ground, and polished without smearing, to give a thin section for microscopic examination in either reflected or transmitted light.

A procedure was developed for encapsulating and impregnating a dried, evacuated sample of triple superphosphate in a mixture containing 47% monomeric styrene, 50% polyester resin, and 3% methyl ethyl ketone peroxide. The effects of rate of polymerization on the quality of the specimen are discussed and the techniques involved in cutting, grinding, and mounting the specimen are given. The resulting thin sections of triple superphosphate on microscopic slides are useful in studying the crystal formation, porosity, and general structure of the particle.
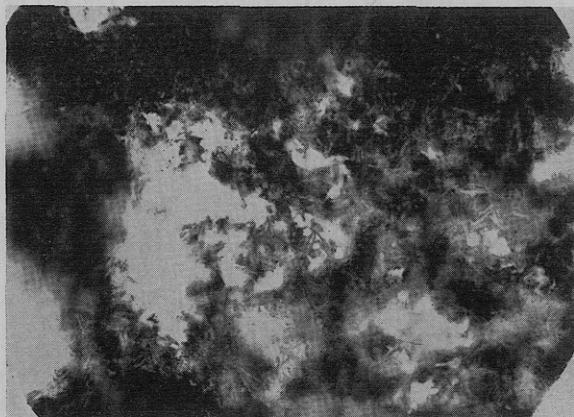
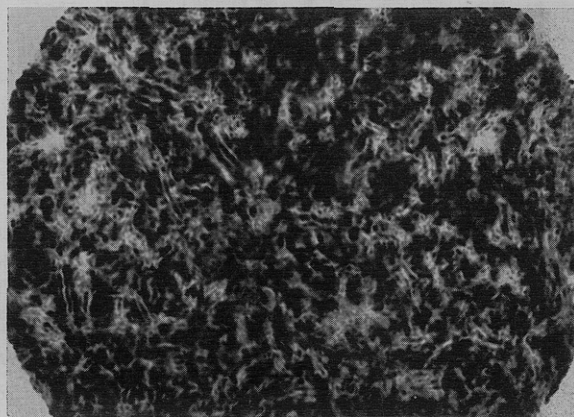Figure 1. Heterogeneous particle structure of triple superphosphate

Figure 2. Homogeneous particle structure of triple superphosphate

Procedure

Mixing of Plastic Materials. A mixture of 50% polyester resin (Laminac Resin 4110, American Cyanamid Co., 30 Rockefeller Plaza, New York 20, N. Y.), 47% monomeric styrene (styrene, The Dow Chemical Co., Midland, Mich.), and 3% methyl ethyl ketone peroxide (Lubersol DDM, Wallace and Tiernan, Inc., 1740 Military Road, Buffalo 5, N. Y.), or a mixture of equivalent materials, is placed in a bottle and stirred or shaken vigorously until the milky color disappears. Less peroxide may be added, depending on the desired rate of polymerization of the mixture. In many cases it is desirable to add less peroxide to prevent crazing of the resin during polymerization. Because of shrinkage during polymerization, slow curing is desirable to minimize strains in the plastic. If the curing is too rapid, the strain birefringence in the plastic interferes with the determination of birefringence in the grains of the sample (1). Lockwood (4) suggests using a dye (Flaming red No. G-305, Ox Color Works, 140 West 42nd St., New York, N. Y.) to give greater contrast between the sample and the resin during microscopic examination of the specimen. This was not attempted here, as it was considered unnecessary in the case of phosphates.

Impregnating the Sample. The phosphate sample is dried at 60° C. for 24 hours before it is impregnated with the liquid resin mixture. If appreciable free moisture is left in the sample, gas bubbles will be formed after the cover glass is placed over the specimen on the slide. The dried sample is placed in a 5-ml. (size 000) porcelain crucible and the liquid resin mixture is poured over the phosphate material until it is completely submerged. The crucible is then placed in a vacuum desiccator and a vacuum of at least 25 inches of mercury is applied. This vacuum is maintained for several minutes or until the bubbling, caused by the air being pulled out of the voids and pores, has stopped. The vacuum is then released slowly until atmospheric pressure is restored. If, after the sample is restored to atmospheric pressure, the resin is absorbed to such an extent that the phosphate material is not completely submerged, additional resin should be added and the sample again subjected to a vacuum. The sample is then allowed to remain at room temperature for at least 12 hours to allow sufficient time for the resin to polymerize. The time required for polymerization may be reduced considerably by curing in an oven at 60° C. After the resin has polymerized, the specimen may be removed by inverting the porcelain crucible and tapping it lightly.

Preparation of Slide. A horizontal slice, approximately $\frac{1}{4}$ inch thick, is cut from the specimen with a hack saw or other fine-toothed saw such as a slow speed metal-cutting band saw. It is necessary to use a slow speed saw to prevent the sample from getting too hot and causing the resin to become plastic. One face of the slice is then prepared for mounting on the petrographic slide. This is done in three successive stages of grinding. Preliminary grinding may be done on a bonded abrasive paper coated with a coarse (No. 120) silicon carbide grit. The paper is placed on a smooth, flat surface and the face of the specimen to be mounted on the petrographic slide is moved uniformly with a circular motion over the grit. Careful manipulation of this grinding operation will prevent the formation of a rounded surface on the face of the specimen. The coarse abrasive is then removed by blowing with dry compressed air. The grinding operation is then repeated with No. 400 silicon carbide paper and the surface of the specimen is finally polished with No. 600 paper. Special care is exercised in cleaning the specimen with dry compressed air after each stage of grinding to remove the coarse abrasives.

Canada balsam is most satisfactory for cementing the specimen to the petrographic slide. Some of the synthetic thermoplastic resins, such as glycol phthalate, have better adhesive properties than Canada balsam, but the balsam requires a lower temperature (100° to 105° C.) to cement the specimen to the slide.

The balsam is cooked slowly (140° to 150° C.) until a sample on the end of a glass stirring rod becomes slightly brittle when cooled. If it is cooked too much, it will become excessively brittle and lose most of its adhesive properties. The petrographic slide is placed on the hot plate at a temperature between 100° and

110° C. and a few drops of cooked balsam are placed on the slide. When the slide has had sufficient time to reach thermoequilibrium with the hot plate, it is removed and placed on an asbestos pad, and the specimen, face down, is quickly placed over the balsam. Enough pressure should be exerted on the specimen to force excess balsam from between the specimen and the slide. After the slide has cooled, the excess balsam around the edge of the specimen is cut away with a razor blade. The exposed face of the mounted specimen is then ground to the required thickness by first using the paper with coarse abrasive (No. 120), then the intermediate (No. 400), and finally the fine (No. 600) abrasive. Careful manipulation of pressure with the fingers will facilitate removal of thick spots and procure a section with fairly uniform thickness. Final grinding of the specimen to the proper thickness and uniformity is determined by inspection for light transmittance under the microscope. It is usually desirable to grind the specimen to a thickness of 0.03 mm. or less.

Applying Cover Glass. A thin coating of flexible collodion (nitrocellulose dissolved in ether) is brushed over the exposed surface of the specimen with a camel's-hair brush to prevent the particles from flowing or separating when the cover glass is applied. A cover glass, 22 mm. in diameter, is placed on the hot plate (100° to 110° C.) and a few drops of cooked balsam are placed on it. The slide with the mounted specimen is inverted and placed face down over the cover glass, then quickly placed on an asbestos pad, and pressure is applied to the cover glass to remove the excess balsam. It is advisable to warm the slide and specimen to approximately 70° C. before the cover glass is applied. This prevents the balsam from getting hard before the cover glass can be seated. Any excess balsam on the slide may be removed with acetone.

Use of Thin Sections. Figures 1 and 2 illustrate the usefulness of thin sections in the microscopic comparison of two triple superphosphates from different sources. The photographs were taken at a magnification of 450 times. Figure 1 shows a distinct crystal formation and a heterogeneous pore size and distribution within the particle, while Figure 2 indicates a lesser degree of crystal formation with relatively good homogeneity of pore size and distribution. Preliminary microscopic comparison of thin sections made in triplicate for each of seven samples from different sources indicate that it may be possible to classify triple superphosphates on the basis of particle structure. Such a classification should be helpful in predicting their behavior in fertilizer processes such as ammoniation and granulation.

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LIQUID FERTILIZER ACIDITY

The Salt Effect in Measuring pH of Liquid Fertilizers with Color-Change Indicators

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The pH of an 8–24–0 liquid fertilizer must be controlled to prevent corrosion of storage facilities, ammonia loss, high salt-out temperatures, and an off-grade product. An inexpensive and convenient method of measuring the pH of a solution is with color-change indicators and commercially available indicator standards. At high salt concentration, as found in liquid fertilizers, a shift in the color-change interval of indicators is observed. This leads to a false measure of the pH of the solution. Theoretical and practical considerations of this indicator salt-effect are discussed.

THE LIQUID fertilizer manufacturer should be constantly concerned with the pH of the product. It is general practice to prepare an 8–24–0 liquid fertilizer by reacting ammonia with phosphoric acid. The pH of this product must be controlled so that the manufacturer can store it in mild steel tanks with a minimum of corrosion. The pH of the ammoniated phosphoric acid solution indicates the ratio of ammonia to phosphoric acid, a necessary bit of information to ensure that a final product is on-grade. A third factor to be considered is the pH-dependence of the solubility of the ammonium phosphate salts in the 8–24–0 product.

For these reasons, the pH of liquid fertilizers should be measured, especially if storage is contemplated. The least expensive method of measuring pH is by use of color-change indicators. It is the purpose of this paper to discuss the factors involved in this type of measurement and to indicate errors which can arise from them.

Theoretical Considerations

Color-change indicators, such as bromothymol blue which is used extensively to measure the pH of liquid fertilizer solutions, are weak acids. Let HIn represent the form of the indicator molecule in acid solution and In⁻, the form in basic solution where the two forms have the characteristic color observed in acidic and basic media. For bromothymol blue, the color of HIn is yellow and In⁻ blue.

The reversible dissociation of acid-base indicators is represented by the equation

$$HIn \rightleftharpoons H^+ + In^- \qquad (1)$$