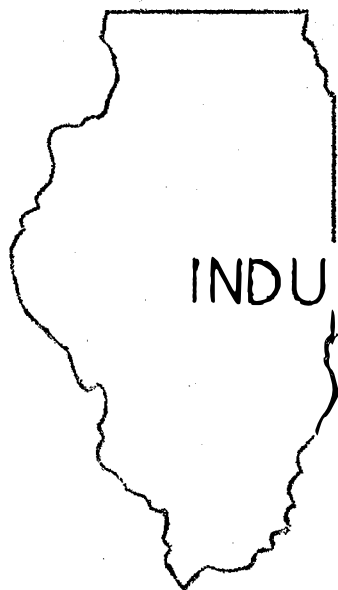


IMN 40

ILLINOIS STATE GEOLOGICAL SURVEY

John C. Frye, Chief Urbana, Illinois 61801

June 1970



INDUSTRIAL MINERALS NOTES 40

COLLOIDAL-SIZE SILICA PRODUCED FROM
SOUTHERN ILLINOIS TRIPOLI

Josephus Thomas, Jr., Henry P. Ehrlinger III, Bruce F. Bohor,
and Robert R. Frost

ABSTRACT

The less than 1-micron fraction of microcrystalline silica from southern Illinois, often called tripoli or amorphous silica, was separated from a fine commercial grade by dispersion in water and centrifugation. The colloid fraction thus collected was then spray dried.

The sized and spray-dried product showed values in several of its physical properties that differed from those measured on the original material. The BET (Brunauer, Emmett, and Teller) surface area of the <1-micron fraction is 2 to 2.5 times greater than the finest commercial grade presently produced, and the modified Gardner-Coleman water adsorption test gave values more than 1.5 times that of the original material. The brightness of the sized and spray-dried product decreased slightly. Scanning electron micrographs clearly show the differences in crystallite size between the two materials and the spherical aggregates resulting from spray drying.

COLLOIDAL-SIZE SILICA PRODUCED FROM SOUTHERN ILLINOIS TRIPOLI

Josephus Thomas, Jr., Henry P. Ehrlinger III, Bruce F. Bohor,
and Robert R. Frost

INTRODUCTION

Tripoli, often referred to as amorphous silica, has been produced in southern Illinois for more than 50 years for use in buffing and polishing formulations and as an extender or filler in paints, rubber, and plastics. This silica is not truly amorphous for it produces an X-ray diffraction pattern typical of that for quartz. With the magnification and depth of focus achievable with a scanning electron microscope, particles are identifiable as porous aggregates of tiny crystallites of quartz, many of which are less than 0.1 micron in diameter.

Tripoli is marketed in a number of sizes. In the finest size, 99 percent of the particles are <10 microns in diameter. Only dry methods have been used in the commercial treatment and sizing of this material, and the <10-micron fraction is the smallest fraction that can be profitably produced by existing dry-process equipment.

A market exists for a still finer product in special filler applications. A recent study (Leamson, Thomas, and Ehrlinger, 1969) indicated that a satisfactory yield of such a product might be recovered from the parent material by a wet process. As crystallites of colloidal dimensions (<2 microns) make up the bulk of the material, a sufficient number of these crystallites (or crystalline aggregates <2 microns) need only be loosened from the larger aggregates and then separated by making use of differences in the sedimentation rates of the various sizes. The study reported here was designed to recover such a product by means of existing technology.

EXPERIMENTAL PROGRAM

The finest commercial grade of microcrystalline silica (99 percent of it <10 microns) was used in this study as a starting material, although a coarser

grade of silica probably would serve as well. Minus 200- to minus 325-mesh starting material, which would not require extensive grinding, should provide a reasonable yield of colloidal particles (<2 microns) if ultrasonic energy were used to break down the loosely cemented aggregates in the more friable mined material, as Leamnson, Thomas, and Ehrlinger (1969) showed. Ultrasonic energy was not used in this study, however, because the starting material was sufficiently fine.

Surface area is the best parameter for comparing the degree of fineness of subsieve particles. The surface area of the starting material used in this study, measured by gas adsorption, was 5.5 to 6.0 square meters per gram. Previous studies indicated that much of this silica is composed of <2-micron particles.

The <1-micron fraction was chosen for evaluation because we thought that the <2-micron fraction would not have sufficiently different properties from those of the starting material and that the <0.5-micron fraction would not provide a sufficient yield. Leamnson, Thomas, and Ehrlinger (1969) showed that the <0.5 fraction has a surface area of 18 or 19 square meters per gram, or 3 times that of the finest grade now produced. We estimated that the <1-micron fraction should have a surface area more than twice that of the starting material.

SEPARATION AND COLLECTION

Four 1-liter centrifuge bottles were each charged with 200 grams of the starting material. The bottles were filled with distilled water and the mixtures stirred to disperse the samples. The samples were then centrifuged for 5 minutes. This period of centrifuging, based on Stokes' Law calculations, left particles smaller than 1 micron in the supernatant suspension. The supernatant liquid was siphoned off the residue and poured into an 8-gallon holding vessel. Because some <1-micron particles are carried down into the residue by larger particles, the residue was redispersed and the centrifugation operation repeated. The residue was then discarded, four more samples were weighed out, and the process repeated.

Three centrifugation runs were conducted with one of the 200-gram samples. The supernatant liquid from each run was evaporated to dryness and the residue weighed. Figure 1 shows the cumulative percentage of the <1-micron fraction recovered from the runs. Forty-four grams of the <1-micron fraction was collected from the 200-gram batch, which was 22 percent of the starting material.

Sufficient material was processed in this manner to yield about 3 pounds of the <1-micron fraction in a rather dilute suspension (stirred daily) in the holding vessels. To thicken the suspension for spray drying, a solution of 1 percent alum and 0.1 percent Separan NP-10 (Dow Chemical Company) was added slowly until flocculation began. After 24 hours, the clear supernatant liquid was siphoned off the flocculated material. The thickened suspension was sent to Nichols Engineering and Research Corporation, Netcong, New Jersey, for spray drying.

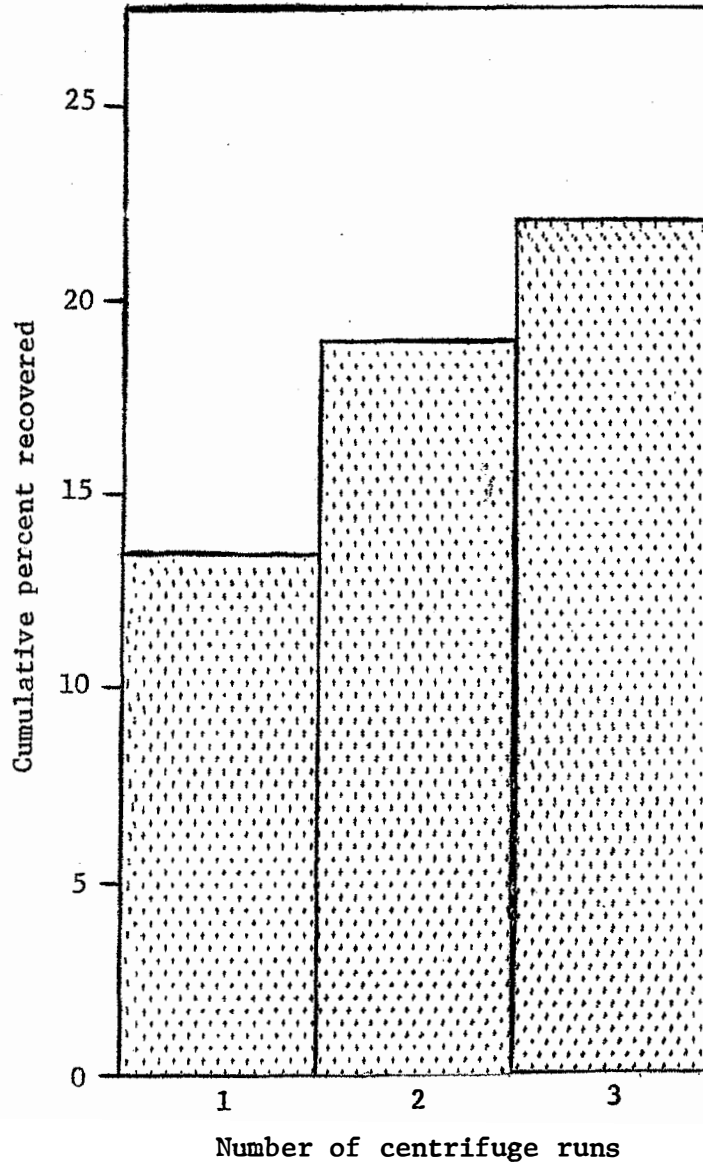


Fig. 1. Cumulative percentage of $< 1\mu$ material recovered from 99 percent $< 10\mu$ starting material.

SPRAY DRYING

Spray drying of a slurry, or thickened suspension, of very fine material has numerous advantages over drying by continuous belt drier, rotary drier, or drum drier. These include purity of product, uniformity of particle size, lack of development of hard aggregates, lower temperature at the mineral surface (which tends to reduce surface oxidation), and better free-flowing characteristics, which make it easier to handle.

Spray-drying methods are particularly successful in recovering dry, soft-aggregate particles from colloidal suspensions. As anyone working with colloids is aware, recovery is not achieved by merely evaporating a colloidal

suspension to dryness and then mechanically breaking up the cake thus formed. Hard aggregates formed by conventional drying cannot be readily redispersed in water.

In spray drying, the slurry is fed directly to the drier in liquid form. Because the feed to the spray drier is atomized, absolute uniformity of drying is achieved. The drying need not be carried out under extremely high temperatures because the moisture in the atomized droplet readily evaporates. Higher temperatures naturally hasten the procedure. The recovery of the product by spray drying is virtually complete.

PROPERTIES OF THE SPRAY-DRIED SILICA

The surface area of the spray-dried silica, determined by gas adsorption was found to be 13.0 to 13.5 square meters per gram (m^2/g). This is 2 to 2.5 times that of the starting material and, of course, reflects the smaller average particle size. The size difference is evident in the scanning electron micrographs of the starting material (fig. 2) and the spray-dried <1-micron fraction (fig. 3). Figure 2 shows the fairly wide range of particle sizes, up to almost 10 microns, occurring in the <10-micron fraction. The sharp edges and flat surfaces of the larger quartz crystals in figure 2 are not evident in the <1-micron spray-dried fraction (fig. 3), in which all the particles are quite uniform in shape and size. The spherical nature of the spray-dried coalesced aggregates also is evident in figure 3. Some of the spherical aggregates are much larger than 1 micron, but they are soft and should be readily dispersed with slight shearing forces.

A simple test demonstrates the relative dispersibility of the spray-dried product compared with that of the starting material. If 5 grams of each material are placed in large-diameter test tubes, which are then filled with water, stoppered, shaken to disperse the solid material, and then allowed to stand 24 hours, approximately half a dozen shakes are needed to redisperse the spray-dried substance that has settled out. On the other hand, 30 to 40 vigorous shakes are necessary to redisperse the settled starting material, which tends to settle out in a rather hard cake.

Modified Gardner-Coleman water absorption tests showed a value of about 48 for the spray-dried material, compared with 29 to 31 for the starting material. The end point is somewhat difficult to interpret for the spray-dried product because continued addition of water causes the wet, solid mass very suddenly to become a wet plastic paste.

G. E. brightness is 86.0 compared with a brightness of 88.5 for the starting material.

SUMMARY AND CONCLUSIONS

A wet process involving spray drying can produce a much finer product from southern Illinois tripoli than the dry processes now being used commercially.

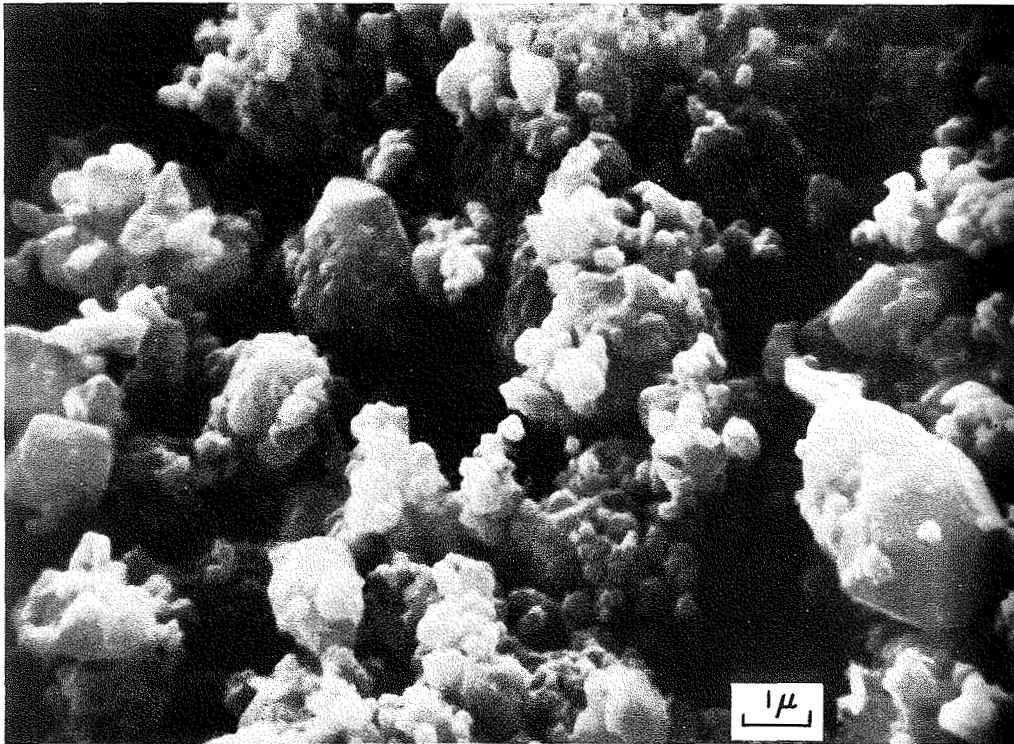


Fig. 2 - Scanning electron micrograph of < 10 micron tripoli ("amorphous" silica).

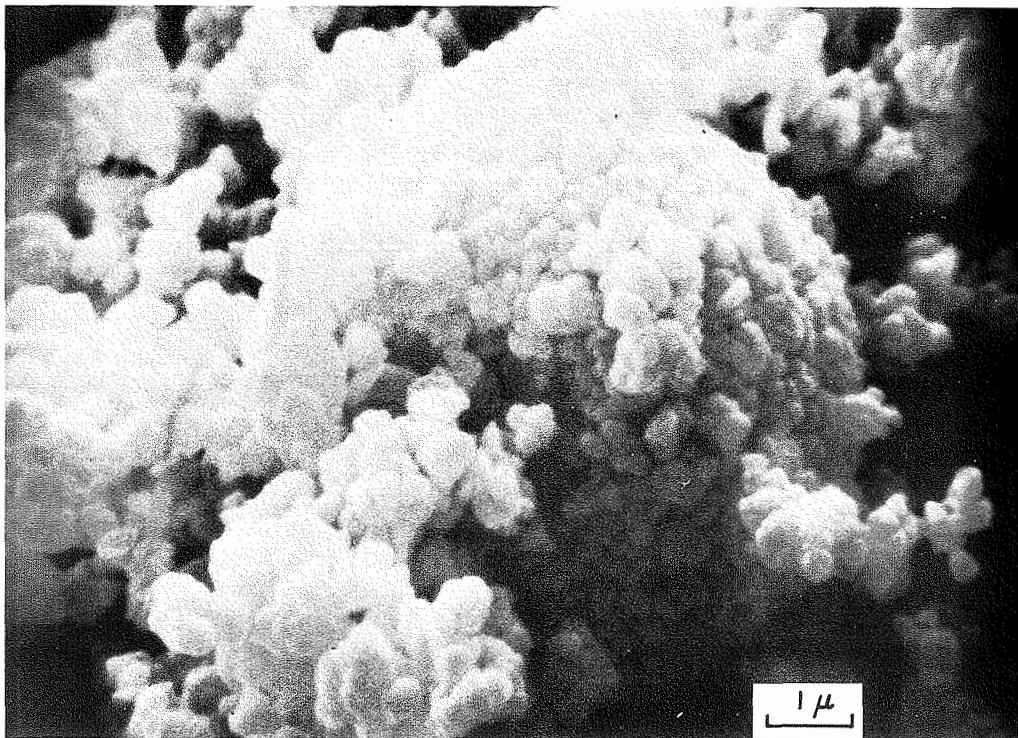


Fig. 3 - Scanning electron micrograph of spray-dried < 1 micron tripoli ("amorphous" silica).

The spray-dried silica is composed mainly of crystallites <1 micron in size. The process is simple. The aggregate crystallites of tripoli are first broken up, either mechanically or ultrasonically. The finer material is then dispersed in water and separated from the larger particles by sedimentation.

The <1-micron separated fraction has a surface area (13.0 to 13.5 m²/g) close to that of Georgia kaolin (16.0 m²/g) and greater than that of the cream and rose tripoli (5 to 12 m²/g) produced in Missouri. A product having an even higher surface area could be produced from this naturally occurring substance if the <0.5-micron size fraction were separated and collected.

Acknowledgments

We thank J. K. Davis and John Dillingham, Illinois Minerals Co., Cairo, for their cooperation in supplying the starting material used in this study and for making water absorption measurements. We also are indebted to Olev Ratsep and William J. Cummins of Nichols Engineering and Research Corporation, Netcong, New Jersey, and Chicago, Illinois, for conducting the spray-drying operation.

REFERENCES

- Leamson, R. N., Josephus Thomas, Jr., and H. P. Ehrlinger III, 1969, A study of the surface areas of particulate microcrystalline silica and silica sand: Illinois Geol. Survey Circ. 444, 12 p.

INDUSTRIAL MINERALS NOTES SERIES

- * 1. Heavy Minerals in Illinois Glacial Sands. 1954.
- * 2. Lightweight Brick from Clay and Peat or Shredded Corncocks. 1955.
- * 3. (1) The Industrial Minerals Industry in Illinois in 1955. (2) Trace Elements and Potash in Some Illinois Gravels. 1956.
4. Subsurface Dolomite in Lake, McHenry, and Part of Northwestern Cook Counties. 1956.
- * 5. (1) Gypsum and Anhydrite. (2) Fluorspar for Controlling Vanadium Staining. (3) Relation of Sulfate and Chloride to Ore Deposits in the Ordovician Rocks of Jo Daviess County. (4) Possibilities for Calcitic Limestone Underground in Kankakee and Iroquois Counties. 1957.
6. Trend in Fuel Uses in Selected Industrial Mineral Products, 1947 and 1954. 1957.
- * 7. Outlying Occurrences of Galena, Sphalerite, and Fluorite in Illinois. 1957.
8. Origin of Illinois Sand and Gravel Deposits. 1958.
- * 9. Shales as Source Material for Synthetic Lightweight Aggregate. 1959.
- *10. Recent Price and Cost Trends Relating to Stone, Sand, and Gravel Production in Illinois. 1959.
- *11. Rare Earth and Trace Element Content of an Unusual Clay on Hicks Dome in Hardin County, Illinois. 1960.
- *12. A Survey of Some Illinois Materials Possibly Useful as Pozzolans. 1961.
13. Summary of Illinois Mineral Industry, 1951-1959. 1961.
- *14. Illinois Stone Production in 1959. 1961.
- *15. Black and Brown Terrazzo Chips from Southern Illinois Limestones. 1962.
- *16. Refractory Clay Resources of Illinois. 1962.
17. Pelletizing Illinois Fluorspar. 1963.
- *18. Permanent Expansion in Bricks. 1964.
19. Binding Materials Used in Making Pellets and Briquets. 1964.
20. Chemical Composition of Some Deep Limestones and Dolomites in Livingston County, Illinois. 1964.
21. Illinois Natural Resources—An Industrial Development Asset. 1964.
- *22. Illinois Clays as Binders for Iron Ore Pellets. 1965.
23. Limestone Resources of Jefferson and Marion Counties, Illinois. 1965.
24. Thermal Expansion of Certain Illinois Limestones. 1966.
25. Annotated Selected List of Industrial Minerals Publications. 1966.
26. Binders for Fluorspar Pellets. 1966.
27. High-Purity Limestones in Illinois. 1966.
28. Illinois Clays as Binders for Iron Ore Pellets—A Further Study. 1966.
29. Clay and Shale Resources of Clark, Crawford, Cumberland, Edgar, Effingham, Jasper, and Vermilion Counties. 1967.
30. Lightweight Bricks Made with Clay and Expanded Plastic. 1967.
31. Clays as Binding Materials. 1967.
32. Silica Sand Briquets and Pellets as a Replacement for Quartzite. 1968.
33. A New Use for Illinois Clay Materials in Pesticide Formulations. 1968.
34. Neutron Activation Analysis at the Illinois State Geological Survey. 1968.
35. Computer-Calculated Lambert Conformal Conic Projection Tables for Illinois (7.5-Minute Intersections). 1968.
36. Beneficiation of Kaolinite Clay from Silica Sand Washings. 1968.
37. Peat and Humus in Illinois. 1969.
38. Kankakee Dune Sands as a Commercial Source of Feldspar. 1969.
39. Alumina Content of Carbonate Rocks as an Index to Sodium Sulfate Soundness. 1969.

* Out of print