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## 3,240,203 METHOD OF DELAMINATING MICA CRYSTALS WITH SONIC VIBRATION

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The present invention relates to a method of delaminating mica flakes. More particularly, the present invention relates to a method of reducing the flake thickness of mica crystals with small solid particles in a liquid medium by exposing the mixture to vibrations of sonic or ultrasonic magnitude.

Mica in single sheet; sheets reconstituted from delaminated flakes, and ground mica is useful in a number of applications including electrical and heat insulators, electron tube spacers, capacitors, furnace and heater windows, paint, and roofing materials. It is often desirable to reduce the overall mica flake size or the flake thickness but not the diameter of the flake so that they can be reconstituted into different shapes. The reduction of flake thickness but not the diameter is commonly called delamination. Prior art methods, including those of grinding, using wet or dry techniques, have proved to be unsatisfactory in that they produce inferior mica-delaminates.

Therefore, it is an object of the present invention to provide an economical and superior method of delaminating mica flakes. Other objects and advantages will be apparent from the following description.

The present method is applicable to both synthetic and naturally occurring micas. These materials embrace the group of mineral silicates crystallizing in monoclinic forms which are capable of being split into thin sheets and flakes. Mica has perfect cleavage in one plane only and mica crystals can be reduced greatly in thickness by delaminating the crystals into very thin leaves or flakes. Because the crystals are not readily cleavable along other planes, the reduction in flake size will occur chiefly parallel to the plane of perfect cleavage.

The aim of this invention has been directed, primarily, in the development of a method for the delamination of synthetic micas, especially fluorophlogopite mica, in such a manner that the resultant delaminated mica be re-formed (i.e. reconstituted) into superior paper or other suitable shape, using no bonding agent other than the mica itself. It is common practice to make sheets of mica using flake mica, or ground mica, by adding some bonding agent such as certain lacquers, glues, cements, plastics, glass, etc. These mica sheets, or boards, have inferior electrical and/or high temperature qualities dependent upon the properties of the bonding agent used as compared to that of mica without such additional bonding agents. Large flakes or sheets of mica are found in nature, but they are rare and the major portion of large, pure sheets of mica have to be imported, primarily from India. These large pure sheets of mica are split into desirable thicknesses and then "punched" with dies to desirable shapes such as used for furnace windows, electron tube spacers, etc.

Synthetic fluorophlogopite (one of several synthetic micas) mica is superior to natural occurring micas (examples: muscovite, phlogopite, biotite) in three ways: (a) better electrical properties, (b) higher thermal stability, (c) the amounts of impurities are generally lower in fluorophlogopite inasmuch as they can be controlled in the synthesis process. However, in the synthesis of fluorophlogopite it is extremely difficult to produce flakes larger than about two inches in diameter. It is apparent for two reasons why a strong reconstituted sheet of mica paper or board with no bonding agents is desirable: (a)

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economical, in that smaller flakes can be delaminated and reconstituted to act as a substitute for the more expensive large sheets of muscovite mica, and (b) that the superior fluorophlogopite may be delaminated and reconstituted to substitute for muscovite mica.

The method described in the invention delaminates mica (natural and synthetic) in such a manner that a superior reconstituted sheet, paper or board may be made as described above. It is not within the scope or aim of this invention to show a method for reconstituting micas, (good methods are already generally known) but to provide an economical and superior method of delaminating mica flakes which can be reconstituted into superior quality forms.

It is well known by those skilled in the art that in aqueous solutions—neutral, acid, or alkaline—cavitation is more pronounced in the temperature zone of 90° F. and above. At 140° F. to 180° F. cavitation is most vigorous (page 10, "Users Reference Guide to the DiSintegrator Ultrasonic Cleaner"). According to the theory set forth in this invention, this range of temperature would be the most desirable, but according to the principles of cavitation, any temperature would suffice as long as the liquid stayed within the temperature limits of its liquid state.

Because water was so readily available, other liquids were not used in the experiments; however, according to the nature of liquids (in that they all have vapor pressure) it is well known that if enough sonic energy is introduced, they will cavitate. Since, in theory, the fine grained particles are accelerated and impelled by the implosion of small bubbles (e.g. cavitation), it is further theorized that any liquid that will cavitate can subsequently be used in this method.

In accordance with the present invention, the delamination of mica flakes is carried out in a liquid medium, preferably in an aqueous medium. However, any liquid will serve as the conductor for transferring energy provided it remains a liquid over a reasonably wide temperature range and is substantially inert to mica and the solid particle materials. The liquid medium acts as a conductor to transfer energy when exposed to vibrations in the sonic or ultrasonic range. In addition to mica flakes, the liquid medium contains small solid particles which are impelled and accelerated by sonic or ultrasonic energies. The action of these small solid particles is to strike and penetrate the edges of the mica flakes in the plane of perfect cleavage causing the crystals to delaminate into thinner flakes.

The solid particles need only be substantially insoluble in the liquid medium to be operative since delamination is purely a mechanical action and not a chemical action. These particles should be in the general size range of colloidal to approximately plus 200 microns, depending upon the thickness of the flake desired. The average size of the calcium carbonate ( $\text{CaCO}_3$ ) particles used is about 5-10 microns. Calcium carbonate is essentially insoluble in water and is readily obtainable in the desirable small fine grain size. Further, calcium carbonate is not so hard that it will grind the mica crystals to any appreciable extent. Another advantage of calcium carbonate is that it can be readily removed and separated after delamination has been carried out.

In theory, when sonic or ultrasonic vibrations are applied to the liquid medium, areas of compression and decompression are formed at approximately the rate of frequency of the sonic energy. The areas of compression and decompression travel through the liquid medium and when the energy is great enough the pressure of the decompression areas will be below the vapor point of the liquid. When this happens, extremely small bubbles will form in these areas of decompression and this occurrence

is known as "cavitation." As the area passes on, the small bubbles implode when an area of compression passes through. This implosion releases a considerable amount of energy and if small solid particles are present they will absorb the energy due to cavitation in the form of kinetic energy and thus be impelled and accelerated.

It is further theorized that for obtaining a 100% delaminated product, the hardness of the small solid particles should be not greater than the mica. Also, the process should be allowed to continue until the flakes are so thin that the particles will not penetrate. In practice, however, it has been found that materials harder than mica will delaminate mica flakes although they are less preferred. Also, the time for carrying out the process will vary widely since some varieties of micas will delaminate more easily under the same conditions than others. For instance, muscovite mica is satisfactorily delaminated to about the same degree as fluorphlogopite although the laboratory time used to carry out the processes can be one and two hours respectively. It will thus be apparent that the time for carrying out the process will depend on the effect desired and the materials used.

Likewise, the temperature is not critical so long as the medium remains liquid, however, optimum temperature for cavitation in water is 90°-180°F. Actual testing has been carried out at room temperature for convenience. Due to absorption of energy by the liquid medium an increase in temperature can be expected. A stirring or agitation device should preferably be used to keep the mixture from setting in the liquid. Also, agitation will enhance complete separation of the delaminated flakes. The stirring can be intermittent or continuous.

The frequency of the sound source is not a primary factor because cavitation can occur at any frequency in the sonic or ultrasonic range, i.e., above about 15 c.p.s. The primary requirement is that the level of energy be great enough to impart enough energy to the small solid particles so that sufficient delamination of mica crystals occurs. Although audible sonic energy can be used to cause delamination, ultrasonic energy lends itself more conveniently for use since it is not an audible irritant.

The amounts of solid particles and mica flakes that should be used in a given amount of water for optimum results will depend on the materials used, frequency and power of the energy source and the amount of agitation used.

#### Example 1

10 grams of fluorphlogopite were added to 10 grams of calcium carbonate. This mixture was placed in an 800 ml. glass beaker with 150 ml. of water. The beaker was then placed in the  $\frac{3}{4}$  gallon tank of the sonic generator. The generator was then turned on and the mixture is stirred intermittently with a glass stirring rod for two hours. The mixture is then taken from the sonic generator and enough hydrochloric acid was added to react completely with the calcium carbonate forming soluble calcium chloride, gaseous carbon dioxide, and water. The delaminated mica was allowed to settle to the bottom of the beaker and the solution was decanted off (an alternative procedure is filtering). The delaminated mica was then washed several times. In the final washing distilled water was used to insure a pure mica product.

#### Example 2

Muscovite mica was much easier to delaminate than fluorphlogopite. Accordingly, using the same conditions and materials as in Example 1, a second experiment was carried out except the time was one hour instead of two.

Due to release of sonic energy and power loss in the transducer the temperature of the solution rose to approximately 110° F.

The actual particle size range of the calcium carbonate ( $\text{CaCO}_3$ ) was unknown. However, a large portion of the particles were in the 1-10 micron range since it is ob-

served that they settled out of water suspension very slowly.

#### Example 3

Approximately 50 grams sodium bicarbonate ( $\text{NaHCO}_3$ ) was used as fine grained solid particles. Sodium bicarbonate is soluble in water, therefore, enough had to be added to the water to saturate it so that by adding more sodium bicarbonate, no more sodium bicarbonate would be dissolved by the water and thus enough of it would stay in solid particle form to cause delamination. 10 grams mica, 100 ml. water were used. Method of agitation was by a glass stirring rod. Time for delamination was one hour, model DR50AH ultrasonic generator was used. The mica flakes were well delaminated.

#### Example 4

5 grams silicon dioxide ( $\text{SiO}_2$ ) was used as fine grained solid particles. 10 grams of mica and 100 ml. of water were added. Time period for delamination was 15 minutes. Method of agitation was by a motor driven stirrer. The resultant delamination was good; however, difficulty was experienced in removing the  $\text{SiO}_2$  from the delaminated flakes.

#### Example 5

50 grams of  $\text{CaCO}_3$  in 750 ml. of water with 50 grams of mica. Time for delaminating, two hours; method of agitation, continuous motor driven stirrer.

In Examples 4 and 5 a DiSontegrator ultrasonic cleaner was used. The average wattage was 80 watts in a  $\frac{1}{2}$  gallon tank. The frequency was 90 kilocycles. The change from 40 kc. (used in earlier experiments) to 90 kc. did not change the resultant delamination to any detectable extent, tending to prove, in part, the theory that any frequency will cause delamination so long as the liquid media will cavitate and small grained particles are present. The use of various small fine grained particles tends to prove that delamination may be achieved with any such small solid particles.

With regard to amounts of wattage necessary for delamination, it has been theorized that the necessary power required is that amount of power necessary to cause cavitation in liquids is dependent on many different factors, and many volumes have been written on this phenomena. Some of the factors are type of liquid, surface tension of the liquid, temperature, amounts of absorbed gases in the liquid, atmospheric pressure, frequency, and many others. In general, the minimum amount of power required to cause cavitation in water is about  $\frac{1}{3}$  watt/cm.<sup>2</sup>. The power used in both generators is well above that range.

The ratios of mica to small particles to liquid given in the examples are those ratios that tend to give the best yield per time necessary for delamination in the laboratory, and not necessarily the best ratios that will give the best results for larger scale commercial production.

In the above examples, the sonic source was a commercial ultrasonic cleaner which develops an average power output of 50 watts of 40 kilocycle energy. The unit uses a pulsed output in order to deliver 200 watts peak power and has an ultrasonic transducer made of barium titanate. The actual device used was model DR50AH made by Acoustics Associates, Inc., of Plainview, New York.

It will be apparent that many variations and modifications within the scope of the herein described method will occur to those skilled in the art. However, the claims of this application are presented with the intention that any variation and adaptation of the principles of this invention are included within the scope of the appended claims.

I claim:

1. A process for delaminating mica comprising placing the mica in a liquid medium containing non-mica solid particles, suspending the mica and non-mica particles while subjecting the medium to vibrations of at least sonic energy of sufficient magnitude to cause cavitation in the liquid for a time sufficient to impel said non-mica particles against

said mica in the plane of cleavage to delaminate the mica into thinner flakes and thereafter separating the resultant product.

2. The process of claim 1 wherein the delamination is carried out while the liquid medium is mechanically agitated.

3. The process of claim 1 wherein the liquid medium is an aqueous medium.

4. The process of claim 1 wherein the solid particles are calcium carbonate.

5. The process of claim 4 wherein the ratio of mica to calcium carbonate is about 1-2:1.

6. A process for delaminating mica comprising placing the mica in a liquid medium containing small non-mica solid particles, suspending the mica and non-mica particles while subjecting the medium to vibrations of ultrasonic energy of sufficient magnitude to cause cavitation in the liquid for a time sufficient to impel said non-mica particles against said mica in the plane of cleavage to delaminate the mica into thinner flakes and thereafter separating the resultant product.

7. The process of claim 6 wherein the liquid medium is an aqueous medium.

8. The process of claim 7 wherein the ratio of water to mica is about 10-20:1.

9. A process for delaminating mica comprising placing the mica in an aqueous medium containing small non-mica solid particles of calcium carbonate, suspending the mica and calcium carbonate particles while subjecting the medium to vibrations of at least sonic energy of sufficient magnitude to cause cavitation for a time sufficient to impel said calcium carbonate particles against said mica in the plane of cleavage to substantially delaminate the mica into thinner flakes and thereafter separating the resulting product.

10. The process of claim 8 wherein the delamination is carried out while the medium is mechanically agitated.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

|           |        |             |       |         |   |
|-----------|--------|-------------|-------|---------|---|
| 2,402,167 | 6/1946 | Lang        | ----- | 241—22  | X |
| 2,468,515 | 4/1949 | Robinson    | ----- | 241—184 | X |
| 2,798,673 | 7/1957 | Kunz et al. |       |         |   |
| 3,034,859 | 5/1962 | Gunn et al. | ----- | 125—24  |   |

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