

## NOTE

### Some effects of grinding kaolinite with potassium bromide

(Received 20 March 1972)

#### INTRODUCTION

THE ADVANTAGES of the KBr pressed-disk technique in the infrared spectroscopic study of clay minerals are well known as also are the danger and remedy of the hygroscopicity of the KBr in the application of this technique (for example, see White, 1971). We have discovered another serious danger in the technique as applied to kaolinite, a danger that has not been reported previously despite the continuing widespread application of the method to that mineral.

The danger occurs in the stage of mixing the kaolinite with KBr before the mixture is pressed into a disk. If that mixing is gentle it causes no effect, but if grinding is used in the mixing, severe changes in the intensities of some of the absorption bands occur due to an interaction between the KBr and the kaolinite. For example, the use of a dental amalgam mixer, such as a Wig-L-Bug, even for very short periods of mixing and especially for the small proportions of kaolinite to KBr used in the disks, causes great changes in the infrared spectrum of the kaolin.

Especially interesting is the ratio of the absorbances of the principal O-H stretching bands at 3695 and 3620  $\text{cm}^{-1}$ . Their ratio,  $R = A_{3695}/A_{3620}$ , is of considerable importance in the classification of kaolinites as shown by Parker (1969) and our discovery relates principally to the effect of grinding-mixing upon it.

#### EXPERIMENTAL

**Materials.** A water-washed kaolinite of 5.5  $\mu$  average particle size with 80 per cent of the particles lying between 2 and 8  $\mu$  in equivalent spherical diameter was used in the principal experiments. The description of the crystallinity and other properties of that kaolinite have been given in an earlier publication (Miller and Oulton, 1970). The potassium bromide was Harshaw Infrared Quality powdered material (i.r. No. G-715). It was dried for seven hours at 100°C and was then stored in a desiccator over Indicating Drierite.

**Apparatus.** The spectrometer and the Wig-L-Bug mixer were the same as described previously (Miller and Oulton, 1970) and the steel vial used to contain the mixtures in the mixer was a hollow right-cylinder 0.5 by 1.0 in. i.d. The two steel balls used in it were 0.25 in. in dia.

**Procedures.** When it was discovered that the mixing effect is sensitive to the proportion of kaolinite to KBr, a fixed amount of exactly 2.0 mg of the kaolinite was weighed out and added to 300 mg of the KBr. The mixtures were then shaken in the steel vial with the steel balls in the Wig-L-Bug mixer for recorded times of different lengths. Each mixture was then pressed at 92,400 psi, the die being pumped before and during the pressing. It, been determined earlier (Miller and Oulton, 1970) that gentle mixing

and the pressing step do not cause the effects observed when the mixing is carried out in the Wig-L-Bug.

Six samples of the same type of kaolinite that had been ground in water (clay concentration, 25% by weight) with 15-30 mesh quartz sand (8 parts to 1 of clay, by weight) for different lengths of time were also studied. After cleaning and drying at 105°C, a pressed disk of each sample was made in two ways, one without Wig-L-Bug mixing, one with 20 sec of the Wig-L-Bug mixing.

Several mixtures containing 1 mg of kaolinite per 300 mg of KBr and one of 60 mg of kaolinite per 240 mg of KBr were also studied. In the latter case, the mixture made in the Wig-L-Bug was diluted by gentle mixing with pure KBr until its concentration was reduced to 1 mg of kaolinite per 300 mg of KBr before pressing into a disk.

One sample was mixed in the Wig-L-Bug without the steel balls and another kaolinite was mixed in a polyethylene vial with polyethylene balls.

#### RESULTS

The absorbance values of the i.r. spectra of the disks were determined by the same base-line procedure described in our earlier publication (Miller and Oulton, 1970). Table 1 shows the  $R$  values calculated from these absorbance values for the standard runs where the steel cylinder and steel balls were used with 2 mg of kaolinite to 300 mg of KBr. In addition, in order to show the individual effects of the mixing on the separate bands, the percentage changes,  $P$ , in absorbance for each of the two bands are given. These  $P$  values were calculated as described earlier (Miller and Oulton, 1970) using the 1002  $\text{cm}^{-1}$  band as reference standard. A band due to sorbed water appeared in the O-H stretch region and in the samples of longer mixing time it was necessary to correct the absorbance values of the 3695 and 3620  $\text{cm}^{-1}$  bands for overlap with that water band.

The rapid and large effect of this mixing-grinding with KBr is apparent. It is also seen that compared with the effect of the percussive grinding in the absence of KBr (Miller and Oulton, 1970), the  $R$  changes are more rapid and, though still principally due to a decrease in intensity of the 3620  $\text{cm}^{-1}$  band, are also due in part to an increase in the 3695  $\text{cm}^{-1}$  band. Furthermore, it is apparent that the decrease in the 3620  $\text{cm}^{-1}$  band is nearly immediate, with little change after 5 sec, while the 3695  $\text{cm}^{-1}$  band first diminishes and then increases rather steadily.

Additional measurements made on the disks after storage in a desiccator for approximately two months show that there is a slight relaxation of the effects, the 3620  $\text{cm}^{-1}$  band going back to normal intensity. It was also noted that there was no sign of destruction of the structure in the spectra of any of the samples, unlike the result of the percussive grinding in the absence of KBr.

Table 1. The  $R$  and  $P$  values for the standard Wig-L-Bug mixing of kaolinite with KBr

Time of mixing (sec) in Wig-L-Bug	$R$	$P_{3695}$	$P_{3620}$
0	1.05		
5	1.18	-6.9	-17.3
10	1.28	+0.9	-17.3
15	1.36	+8.7	-16.2
20	1.45	+6.2	-23.1
30	1.46	+8.1	-22.0
50	1.47	+16.4	-17.0

Table 2. The  $R$  values for wet-ground kaolinite with and without Wig-L-Bug mixing

$R$		
Hours of wet-grinding	Without Wig-L-Bug	With Wig-L-Bug (20 sec Each)
1	1.09	1.63
2	1.10	1.64
3	1.16	1.71
4	1.13	1.80
5	1.13	1.90
6	1.14	1.97

Mixtures containing the lower proportion of kaolinite to KBr (1-300) showed essentially the same results, but even more rapidly. When the proportion of clay to KBr was 60-240, the effect was correspondingly diminished, 20 sec of the mixing-grinding producing an  $R$  value of only 1.14. For the kaolinite mixed without the steel balls,  $R$  went from 0.95 to 1.03 in 5 sec. The plastic chamber and plastic balls were used with a kaolinite that initially had  $R = 1.32$  and brought the value to 1.81 in 20 sec.

The results for the wet-ground samples are given in Table 2. It appears that wet-grinding produces only a small effect on  $R$ , but renders the kaolinite more susceptible to the action of KBr.

#### DISCUSSION

Parker (1969, see also van der Marel and Krohmer,

1969) has recently stressed the importance of the  $R$  value as an index for the classification of kaolinites. He was able to show a useful correlation between the  $R$  value and the crystallinity and shape of the kaolinite. He was also able to show that for samples of kaolinite dispersed in KBr increase in the aspect ratio of the particles increased the  $R$  value, especially by increase in the intensity of the 3695  $\text{cm}^{-1}$  band. He did not describe the intensity of the grinding used in preparing these dispersions. In view of his findings, one might be inclined to explain our results as due in part to a delamination of the kaolinite particles by the KBr, possibly aided by an intercalation of the kaolinite by the water sorbed during the mixing. We found no evidence for destruction of the lattice.

More work will be needed to explain the large effect observed. It is unfortunate that corroborative studies of the action of the KBr would depend on the difficult separation of the kaolinite from the large proportion of KBr without changing the condition of the kaolinite during the separation process.

*Acknowledgements*—The authors wish to express their appreciation of helpful discussions with C. G. Albert, E. W. Greene, W. L. Haden, Jr., and J. C. Lim.

*Department of Chemistry* JOHN G. MILLER  
*University of Pennsylvania* T. DIXON OULTON  
*Philadelphia, Pa. 19104, U.S.A.*

*Engelhard Minerals and Chemicals Corp.*  
*Menlo Park*  
*Edison, New Jersey 08817, U.S.A.*

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