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Letters to the Editor

Sir:

We refer to the paper "Adsorption of β-Carotene: II. On Cation Exchanged Bleaching Clays," by K.Y. Liew, S.H. Tan, F. Morsingh and L.E. Khoo (*JAOCS* 59:480 [1982]), in which the authors make the statement:

> "In addition to small amounts of quartz and mica, Filtrol and Fulmont clays contain a substantial amount of kaolinite."

The authors base this statement on their interpretation of the X-ray powder diffractogram for Filtrol 105. Later in the article, they explain the apparent disappearance of kaolin from the X-ray powder diffractogram of ion-exchanged Filtrol 105 as follows:

> "After cation exchange and heating to 450 C, the 3.52Å d spacing in Filtrol and Fulmont disappeared, indicating that the kaolinite mineral in these clays had become amorphous."

We must respectfully disagree with the authors concerning their interpretations regarding Filtrol 105 bleaching clay. In fact, it contains no observable kaolinite – and certainly no "substantial amounts" of this material.

We believe the authors have misassigned their 3.52Å peak to kaolinite (3.58Å) when, in fact, it should have been assigned to the 3.50Å anhydrite ($CaSO_4$) peak. Anyhydrite, we know, is present as a minor constituent. As further evidence that this is the correct interpretation, we note: (a) that kaolinite should have an equally intense basal peak at 7.15Å which is, in fact, absent from their pattern and (b) that a second, low-intensity anhydrite peak at 2.86Å is present.

Our explanation for the disappearance of the 3.50Å peak is that it occurs by simple dissolution of the slightly soluble anhydrite phase during the washing steps performed by Liew et al., prior to ion exchange. In Figure 1, we show three X-ray powder diffraction patterns for Filtrol 105. Sample A has been dried to 100 C (but not washed). Sample B has been heated to 450 C for 4 hr (but not washed), and sample C has been washed, filtered, then dried at 100 C.

Clearly, the disappearance of the 3.50Å peak is not due to a thermally induced transition to an amorphous material as suggested by Liew et al. since sample B (calcined at 450 C for 4 hr) remains unchanged from sample A (dried at 100 C for 2 hr). Furthermore, sample C (washed and dried) shows convincingly that simple washing and drying is quite sufficient to remove the anhydrite peaks (3.50Å, 2.86Å spacings) from the X-ray diffraction pattern.

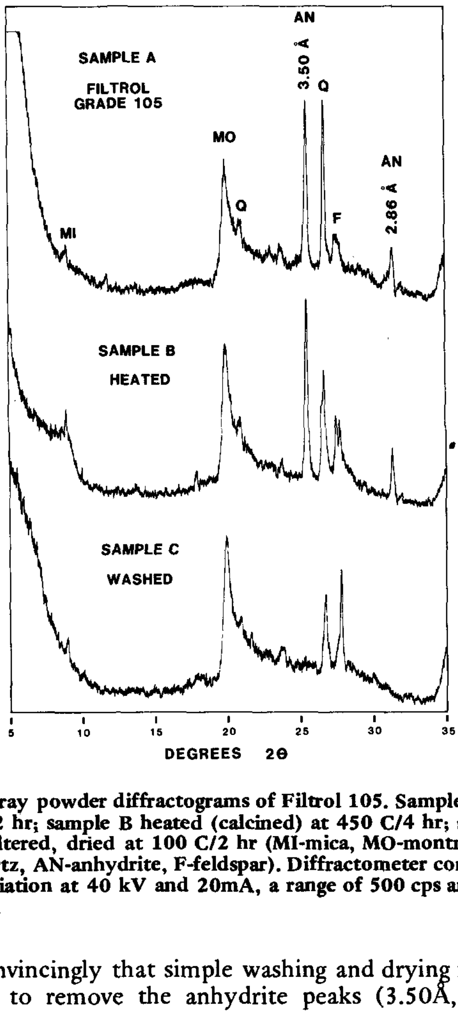

FIG. 1. X-ray powder diffractograms of Filtrol 105. Sample A dried at 100 C/2 hr; sample B heated (calcined) at 450 C/4 hr; sample C washed, filtered, dried at 100 C/2 hr (MI-mica, MO-montmorillonite, Q-quartz, AN-anhydrite, F-feldspar). Diffractometer conditions: Cu $K\alpha$ radiation at 40 kV and 20mA, a range of 500 cps and a rate of 1C/min.

Because anhydrite, a byproduct of the acid-activation process, is an intense reflector of X-rays at the 3.50Å spacing, relatively small amounts of this material give a quite noticeable peak when mixed with montmorillonite. We estimate its amount at 5% or less in a typical sample of Filtrol 105.

TABLE I

Gr 105 Decolorization Efficiency as a Function of Dehydration Temperature

Dehydration temperature (C)	Vm(%)[a,b]	Lovibond Red[c]
–	28.7	3.36
Gr 105	23.1	3.26
25/64 hr	15.2	3.42
50/64 hr	11.4	4.18
112/64 hr	10.7	4.23
450/4 hr	6.2	5.51
450/64 hr	5.0	6.73

[a] Vm (volatile matter) is equivalent to loss on ignition at 1,000 C.

[b] The sample with a Vm of 28.7% was prepared by allowing a sample of the Gr 105 product (Vm of 23.1%) to be exposed to water vapor at 100% relative humidity at ambient temperature for 42 hr. The remaining samples were derived from the aforementioned sample and were dried further under normal atmospheric conditions at their respective temperatures for the times indicated.

[c] Contacts carried out under atmospheric conditions at a 5.0% clay dosage level (as-is basis) in crude palm oil at 248 F for 10 min. Lovibond Red values correspond to measurement in a 5.25" cell. Higher Lovibond Red numbers indicate darker (less decolorized) oil.

One other point made in this paper requires comment. The authors conclude Fulmont is the most active clay followed by Filtrol and then Galleon. While we would not disagree with this ranking under the experimental conditions employed (clays heated to 450 C for 4 hr prior to adsorption studies; β-carotene adsorption from acetone solution at room temperature), we would argue that this ranking could easily change under the more realistic conditions generally practiced by the industry (i.e., clays used at dehydration levels as optimized by producer; complex mixture of carotenoids adsorbed from hot oils under partial vacuum). Table I shows, for instance, how heating to 450 C affects the ability of Filtrol 105 to bleach (decolorize) crude palm oil. It can be surmised from these data that calcining 450 C prior to use does not constitute the optimum pretreatment conditions for utilizing this product.

Our purpose in drawing attention to these otherwise minor technical points stems from our intense desire to maintain our reputation as a trusted and dependable supplier of high quality acid-activated bleaching clays to the vegetable oil refining industry. Our comments should, in no way, detract from an otherwise interesting and stimulating paper.

Sincerely,
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D.B. JENKINS
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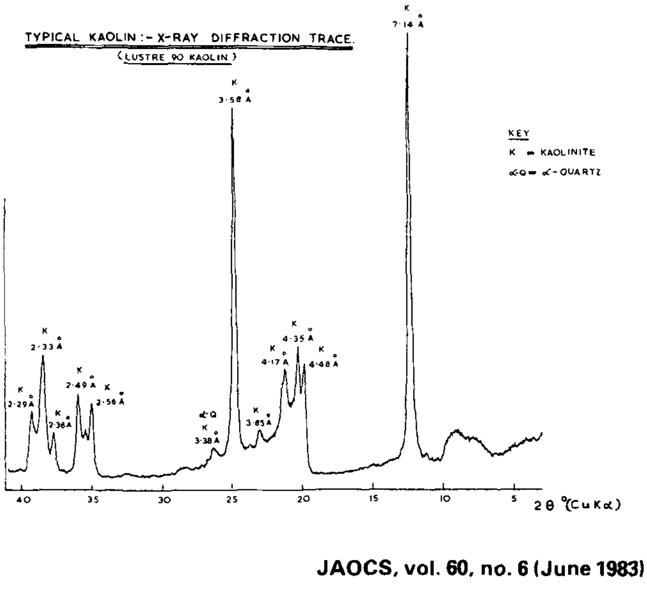
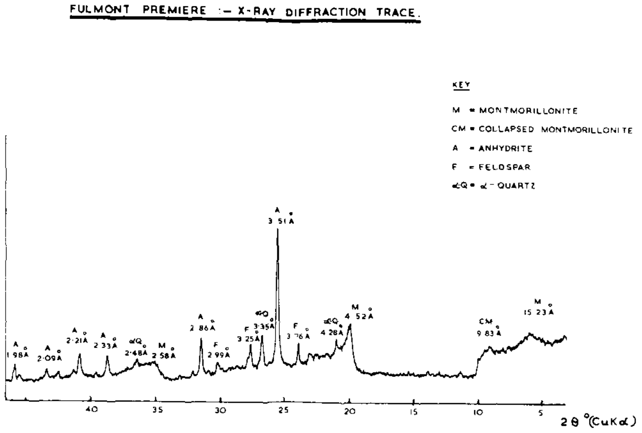
Sir:

In the paper "Adsorption of β-Carotene: II. On Cation Exchanged Bleaching Clays," by K.Y. Liew, S.H. Tan, F. Morsingh and L.E. Khoo (*JAOCS 59*:480 [1982]), reference is made under the results and discussion section to the composition of acid-activated bleaching earths as determined by X-ray diffraction. For the commercially available products, Filtrol and Fulmont, Liew et al. state that they consist mainly of montmorillonite with traces of quartz and mica and substantial amounts of kaolinite.

As manufacturers of the acid-activated bleaching clay Fulmont, we strongly dispute the identification of kaolinite as a substantial component of this product which is based on a high purity English natural calcium montmorillonite. Although no X-ray diffraction trace is given for a Fulmont clay, the trace obtained in our laboratories for this product is very similar to that given for Filtrol in Figure 1b in the above paper. We believe that Liew et al. have misinterpreted the line at 3.52 Å as due to kaolinite. We support our contention by appending our X-ray diffraction traces for Laporte grade Fulmont Premiere and for a commercially available purified kaolinite clay (Kaolin Lustre 90) and by noting that: (a) the first main kaolinite line (001) at 7.15Å is completely absent from all traces given in Figure 1 of the paper by Liew et al.; (b) the second main kaolinite line (002) is normally at 3.57Å, not 3.52Å as given in Figure 1; (c) it is extremely unlikely that kaolinite would become amorphous by the washing procedure used to cation exchange the acid-activated bleaching earths.

We argue that the line at 3.52Å in the Filtrol sample and by inference in the Laporte Fulmont acid-activated bleaching earth is due to the presence of small quantities of well crystallized anhydrite (anhydrous calcium sulfate) left behind as a partially insoluble byproduct of the acid-activation process and formed by the reaction of the calcium in the montomorillonite and the sulfuric acid used for activation. This argument is supported by evidence of other peaks due to anhydrite on the X-ray diffraction trace in Figure 1b in the paper by Liew et al., on our enclosed trace for Fulmont Premiere and by the absence of the 3.52Å peak on the traces Figure 1c to 1f for clays which have been washed with large volumes of water during the exchange process. This washing process has been sufficient to dissolve and remove the anhydrite (solubility 0.2g per 100 mL water at 20 C) from the acid-activated bleaching earth.





As one of the world's major manufacturers of acid-activated bleaching earths based on montmorillonite, we are very concerned about the ease with which X-ray diffraction traces as published in the paper by Liew et al. can be misinterpreted. We would recommend the use of a trace covering a wider range of 2 θ angles and consultation with a recognized clay minerals expert regarding trace interpretation. We are also concerned that a journal of your reputation can allow publication of a refereed paper of this type with the errors it contains without reference to an appropriate authority.

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Widnes, Cheshire
England

Sir:

We are grateful to Dr. M.H. Yates in pointing out our misinterpretation of the 3.52Å peaks in the X-ray diffraction patterns reported in *JAOCS* 59:480 [1982]. As the composition of the bleaching earths is secondary to our adsorption studies, we overlooked the absence of the 001 peak. We are however glad that Dr. Yates has been able to confirm some of our experimental results.

We apologise for our misinterpretation.

Sincerely yours,

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