SCIENTIFIC SUB-COMMITTEE
-
12th Session
-

40.809 E

O. Eng.

SC-3

Brussels, 12 December 1996.

PROPOSAL BY THE EC FOR THE AMENDMENT OF HEADING 25.07
(Item II.10 on Agenda)

Reference documents :

40.038 (RSC/13)
40.180 Annex C/15 (RSC/13 - Report)
40.207 (SSC/11)
40.460 Annex A/5 (SSC/11 - Report)
40.255 (RSC/14)
40.470 Annex A/11 (RSC/14 - Report)
40.413 para. 24 (HSC/18)
40.600 Annex E/1, para.13 (HSC/18 - Report)
40.756 (SSC/12)

On 25 November 1996, the Secretariat received the following comments from the Canadian Administration on the infrared analysis of kaolinites of heading 25.07.

I. CANADIAN COMMENTS ON THE INFRARED ANALYSIS OF KAOLINITES OF HEADING 25.07

A Background

The EC has proposed that heading 25.07 (Kaolin and other kaolinic clays) be divided into two subheadings, namely "kaolin" and "other kaolinic clays". The Canadian Administration asked that this issue be referred to the Scientific Sub-Committee (SSC) to ensure that these two groups of products can be distinguished from one another.

File No. 2593

At the 11th Session of the SSC, the French Delegate provided a copy of pages 18 to 21 of the text "Clay Mineralogy : Spectroscopic and Chemical Determination Methods", edited by M.J. Wilson, published by Chapman and Hall.

40.809 E

Discussion

The above reference indicates that the various kaolin clays can be distinguished from one another by their infrared (IR) spectra. The reference further states that a number of collections of IR spectra of minerals exist. However, none of these collections is perfect, incorrect identification or impurities being not uncommon. Indeed, we are concerned about the quality of the spectrum for dickite located on page 19 of the text by M.J. Wilson. Broadening in the 1100 cm-1 area may be caused by the presence of silica and therefore not characteristic of dickite. Also, the reduced peak separation in the area 1033 to 935 cm-1 and 534 to 423 cm-1 (as compared to the kaolinite spectrum) may be caused by a larger amount of sample (start of saturation of the IR absorption) .

The authors indicate that the spectrum of disordered kaolinite suggests that such disorder could arise from a small amount of dickite and/or nacrite-like stacking in the kaolinite structure. If references are not certain as to which species are present, then the quantitative determination of each species by this method would not be feasible.

In order to get a better understanding of the range of kaolin products available and to apply the IR analysis described in the reference mentioned in paragraph 2 above, we contacted four North American kaolin clay producers and obtained samples and some documentation for 19 different commercial products.

The documentation describes the products as kaolin clays or ball clays. It does not provide any information on the presence or relative abundance of any of the kaolin sub-species.

All samples obtained were run on a Fourier transform IR (FTIR) by KBr and were compared with the reference spectra found on pages 19 and 20 of the reference mentioned above.

None of the samples produced an exact match with the reference standards. The spectrum of Snobrite Special from Evans Clay USA (Annex 1) is typical of most spectrum we obtained. This spectrum is intermediate between kaolinite and dickite (most apparent in the ratios of the peaks at 3693 - 3624 cm-1 and 792 - 755 cm-1). Both types of ordering are significant. The peak ratios suggest that dickite is the predominant constituent. This seem anomalous since the author of the same reference states (page18) that dickite and nacrite are rare.

Other clays proved to be more complex. The spectrum for L-1 from Kentucky-Tennessee Clay (Annex 2) displays both kaolinite-dickite ordering and a significant amount of silica (in the order of 40 % by weight based on the elemental composition).

The spectrum of a calcined kaolin clay (e.g., Ansilex 93 from Englehard USA - Annex 3) is very different from the spectrum of a non-calcined clay.

The remaining IRs and the documentation relating to the samples that we have obtained will be forwarded to the Secretariat and will be available for review during the up-coming session of the SSC.

Conclusion

The various members of the kaolin clay family are very similar. The 19 samples examined demonstrate that commercial products are frequently composed of mixtures of kaolinic species. Although IR analysis permits the identification of kaolinite and dickite ordering within commercial kaolin clay samples, available references do not provide a means of determining the relative amounts of each.

2.

Nomenclature Comments

Our review of these products has indicated that kaolin refers to the clay family which contains the members kaolinite, dickite, nacrite, anauxite and halloysite-endellite. Thus the present text of heading 25.07 contains a redundancy and should be amended.

We would suggest either of the following :

- KAOLINITE AND OTHER KAOLINIC CLAYS, WHETHER OR NOT CALCINED ; or

- KAOLINIC CLAYS, WHETHER OR NOT CALCINED.

The Explanatory Notes and the EC proposal, if accepted, should be changed accordingly.

17. The list of clays analysed by the Canadian Administration, and the three annexes mentioned in paragraphs 9, 10 and 11 above are set out in Annexes I to IV to this document, respectively. The remaining IRs and documentation (see paragraph 12 above) will be made available for reference during the meeting.

18. The reference IR spectra concerning kaolinite and other kaolinic minerals given in "Clay Mineralogy" (edited by Mr. M.J. Wilson) discussed by the Canadian Administration (see paragraphs 3-5 above) are reproduced at Annex V to this document.

II. SECRETARIAT COMMENTS

19. As indicated in paragraph 14 of Doc. 40.756, technical literature shows that "kaolin" consists principally of the mineral kaolinite. If "other kaolinic clays" consisted principally of kaolin minerals other than kaolinite (e.g., halloysite), the technical information given in paragraphs 8 to 12 of the same document could give an answer to the question of whether "kaolin" can be distinguished from "other kaolinic clays".

20. The Secretariat understands from the comments of the Canadian Administration that such a distinction would become difficult by infrared spectroscopy when kaolinite contains other kaolininc minerals (e.g, dickite, nacrite or both). After analysing 19 different samples, the Canadian Administration also came to the conclusion that commercial kaolin is frequently composed of mixtures of kaolinic species as the infrared spectra of these samples were not exactly matching with the reference spectra of the individual minerals (see Annex V). It is also pointed out that these reference spectra are not perfect due to impurities in samples or incorrect identification.

21. As regards the nature and composition of kaolin, the Secretariat has found the following additional information in technical literature :

(i) In its natural state kaolin is a white, soft powder consisting principally (emphasis added by the Secretariat) of the mineral kaolinite... Kaolin as found in nature usually contains varying amounts of other minerals such as muscovite, quartz, feldspar, and anatase. In addition, crude kaolin is frequently stained yellow by iron hydroxide pigments. It is often necessary to bleach the clay chemically to remove the iron pigment and to wash it with water to remove the other minerals in order to prepare kaolin for commercial use ("Britannica", 15th Edition, Micropaedia, volume 6, p. 730 and Macropaedia, volume 24, p. 207).

(ii) Clays containing a preponderance of the clay mineral kaolinite are known as kaolinitic clays. Several commercial clays are composed predominantly of kaolinite. These are china clays, kaolines, ball clays, fireclays, and flint clays. The terms china clay and kaolin are used interchangeably in industry. China clays are high-grade white kaolins...(some) deposits are composed almost wholly of the mineral kaolinite...@ (The AEncyclopaedia of Science and Technology@, vol.3, page 229).

22. Thus it appears that kaolin, though consists principally or almost wholly of the mineral kaolinite, could have other impurities in the form of minerals. However, the Secretariat is not certain whether these include other kaolinic clay minerals such as dickite and nacrite. As pointed out by the Canadian Administration, there are indications in technical literature (Clay Mineralogy, edited by Mr. M.J. Wilson) that disorder in the infrared spectra of kaolinite could arise from a small amount of dickite and/or nacrite-like stacking in the kaolinite structure. In such cases, it would become difficult to establish by the infrared spectroscopy whether the principal ingredient is kaolinite or other kaolinic minerals. It is not clear whether the other known test methods (X-ray diffraction, electron microscopy) would also pose similar problems. The Sub-Committee is requested to consider this aspect while examining possible test methods for distinguishing between kaolin and other kaolinic clays.

23. As regards the Canadian proposal for amending the legal texts, the Secretariat wonders whether it is necessary to amend the present texts since no difficulty has been reported in the past. In this connection, the Secretariat also wonders whether the samples tested by the Canadian Administration (ball clays) were technically the same as Akaolin@, which is known as china clay in the industry (see paragraph 21 (ii) above).

III. CONCLUSION

24. The Sub-Committee is requested to take into account the above comments by the Canadian Administration and of the Secretariat when discussing the question of providing objective criteria for distinguishing between kaolin and other kaolinic clays.

x x x