



SCIENTIFIC SUB-COMMITTEE

NS0045E1
(+ Annexes I and II)

-
17th Session
-

O. Eng.

Brussels, 6 December 2001.

CLASSIFICATION OF CERTAIN ACID-ADDED CLAY PRODUCTS

(Item II.8 on Agenda)

Reference documents :

NC0404E1 (HSC/27)
NC0430E2, Annex IJ/5 (HSC/27 – Report)

I. BACKGROUND

1. At its 27th Session, the Harmonized System Committee held a preliminary discussion on a question raised by the Colombian Administration concerning the classification of the “Pure-Flo B81”, “Pure-Flo Pro-Active” and “Pure-Flo Color Master” clay products, obtained by controlled addition of sulfuric acid to natural palygorskite (attapulgite)-smectite clay through a process patented in the United States (Patent No. 5,783,511, date of patent : July 21, 1998).
2. The HS Committee unanimously concurred with the views expressed by the Secretariat in paragraph 19 of Doc. NC0404E1 that this question should be submitted to the Scientific Sub-Committee at its next session. In addition to responding to the questions raised by the Secretariat in paragraph 18 of Doc. NC0404E1, the Sub-Committee was asked to give its views as to whether adding acid to these products for the specified purposes was covered by the term “washing” for purposes of Chapter 25. Also, as proposed by the Secretariat (paragraph 20), samples of the products at issue should be obtained and analysed by the Customs laboratories of Contracting Parties, and the results of those analyses submitted to the Sub-Committee as further information.

II. SECRETARIAT ACTION AND COMMENTS

3. Acting upon the HS Committee’s instructions, on 7 June 2001, the Secretariat requested the Colombian Administration to send samples of the “Pure-Flo B81”, “Pure-Flo Pro-Active” and “Pure-Flo Color Master” clay products to the Secretariat as soon as possible.

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4. Although a reminder was sent to the Colombian Administration on 19 October 2001, no response has been received by the time of the preparation of this document.
5. A brief description of the patented process and the Secretariat comments on the subject matter were given in paragraphs 2 and 8 to 20 of Doc. NC0404E1, respectively. The technical documentation referred to in paragraph 4 of the same document will be made available to delegates during the session (English and Spanish only). The Secretariat is of the view that the following information extracted from the aforementioned patent and from the letter of the importing company to the Colombian Administration is particularly relevant to the discussion by the Sub-Committee :

From U.S. Patent 5,783,511

- 5.1. "...Optimized acidification of a palygorskite-smectite clay mineral is depicted graphically in FIG.1 where the ordinate is surface acidity (SA) for a clay mineral, expressed as milliequivalents of acidity per gram and the abscissa is the amount of added acidity (A), also expressed as milliequivalents of acidity per gram.
- 5.2. Acidification of the palygorskite-smectite clay mineral is effected by adding sulfuric acid to the clay mineral in an amount not to exceed about 1.5 milliequivalents of acidity per gram of produced bleaching clay product. Preferably the amount of sulfuric acid is about 0.5 to about 1.5 milliequivalents of acidity per gram of bleaching clay product (measured on a dry basis), more preferably about 0.75 to about 1.25 milliequivalents of acidity per gram of bleaching clay product. Sulfuric acid may be added as an aqueous solution or as concentrated sulfuric acid. The term "sulfuric acid" refers herein to either an aqueous solution of sulfuric acid or concentrated sulfuric acid.
- 5.3. The addition of sulfuric acid to the palygorskite-smectite clay mineral can be achieved in any convenient manner. For example, sulfuric acid may be added by spraying sulfuric acid onto an agitated particulate clay mineral bed, by adding aqueous sulfuric acid to a clay mineral as it is passed through a pug mill, and the like.
- 5.4. The resulting bleaching clay product is not washed with water, but instead is dried and comminuted to a desired particle size.
- 5.5. The addition of sulfuric acid is effected so as to maintain a substantially constant ratio of surface acidity to added acidity for the produced bleaching clay product. Surface acidity is calculated as the difference between total acidity (acidity of a clay suspension) and solution acidity (acidity of a water extract of the clay suspension).
- 5.6. The addition of sulfuric acid so as to maintain a substantially constant ratio of surface acidity to added acidity is illustrated in FIG. 1, where the slope of the depicted curve is substantially constant until the added acidity exceeds about 1 milliequivalent per gram of bleaching clay product. Further addition of sulfuric acid does not result in an increase of surface acidity, the desired acidity for bleaching, but instead increases the likelihood of structural deterioration of the clay mineral structure..."

"FIG. 1" (Figure 1) referred in subparagraphs 5.1 and 5.6 above is reproduced in Annex I to this document for the information of the Sub-Committee.

From the importer's letter

- 5.7. "...Surface area analysis and mineralogical analysis was used to demonstrate the differences between raw materials, "acid-added" products and "acid-activated" products.
- 5.8. Surface area analysis : The surface analysis includes the BET-nitrogen surface area, total pore volume and average pore diameter. This determines the amount of internal and external surface area and porosity available for the removal of pollutants (chlorophyll, colour, etc.). The X-Ray Diffraction analysis was used to determine the mineral phases present in each material.
- 5.9. Results of the surface area test : The properties of the surface area of the "acid-added" products were similar to those for the "natural B80 Pure-Flo product". The minimal differences were normal, and are the result of the location of the raw material in the mine. However, "acid-activated" clay typically has a larger surface area, larger pore volume and smaller average pore diameter than "acid-added" products. The results can be seen in the chart below :

BET Nitrogen Test	Calcium bentonite raw material	Acid-activated Calcium bentonite	Pure-Flo B80 Natural	Pure-Flo B81 Acid-added	Pure-Flo Pro-Active Acid-added	Pure-Flo Colormaster Acid-added
Surface area (m ² /g)	79.2	325.4	138.9	147.7	143.9	131.4
Pore volume (cc/g)	0.1380	0.4700	0.3513	0.4351	0.3522	0.3499
Average pore diameter (nm)	7	5.8	10.1	11.8	9.8	9.0

- 5.10. The chart shows the comparison between surface areas of clays before and after being treated by additives or activation with acid. The surface area analysis is good for determining whether there have been changes in the structure of the clay. Note therefore how the surface area of the bentonite increases almost fivefold after being acid-activated, while Oil-Dri products show only marginal changes after acid has been added.
- 5.11. Mineralogical analysis : We attach four sheets with graphs from the results of the X-Ray Diffraction tests. The principal components of each clay are smectite (montmorillonite) and attapulgite (palygorskite). Graph 1 shows the comparison of results of diffraction for each Oil-Dri products – B80, B81, Pro-Active and Colormaster. A study of this shows that the clay part in the neutral clays (B80) and in "acid-added" clays is similar. The gypsum found in the B81, Colormaster and Pro-Active products is the result of the reaction between the calcium in the clay and the sulfuric acid. Quartz is common to all samples. The individual mineralogy of each product is shown in Graphs 2, 3 and 4..."

The four graphs referred to in sub-paragraph 5.11 are also set out in Annex II to this document.

6. The Secretariat is not sure whether the information given in Doc. NC0404E1 and above will suffice to enable the Sub-Committee to give its advice on the questions referred to it by the HS Committee.
7. If the Secretariat succeeds in obtaining samples of the products under consideration from the Colombian Administration and to have them analyzed by a Member Customs laboratory before the session, the analytical results will be submitted to the Sub-Committee in an additional document.

III. CONCLUSIONS

8. Taking into account the information and comments given in Doc. NC0404E1 and above, the Sub-Committee is invited to express its views as to :
- (a) Whether or not "addition of acid" to the products of Chapter 25 without modifying their chemical or crystalline structure, in general, and to the "Pure-Flo" products in question, in particular :
 - (i) is covered by the expression "washing with chemical substances"; and/or
 - (ii) could be regarded as a process normal to these products,
within the terms of Note 1 to Chapter 25.
 - (b) On the basis of the response given to the above question, whether the products at issue would be covered by heading 25.08 or by any other heading of the Nomenclature (e.g., heading 38.02); and
 - (c) On the basis of the responses to the previous two questions, whether there is a need for any amendments to the Nomenclature and/or the Explanatory Notes or to the Compendium of Classification Opinions.
9. If the information available so far is not sufficient to respond to the questions posed above, the Sub-Committee is requested to express its views as to whether the product samples should be obtained from the United States.

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