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Asbestos in toys: an exemplary case

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ABSTRACT

Background *DAS was an artificial clay which, once molded, hardened at room temperature. It was largely used as a toy between early 1960 and 1975. It was produced and sold in Italy, Netherlands, Germany, UK and Norway.* **Objectives** *Describing and reporting the presence of asbestos in a toy.* **Methods** *The presence of asbestos in DAS was investigated by light and electron microscopy on samples of the original material. Administrative documents were searched at the State Archives of Turin. Interviews were carried out with past employees on annual production, suppliers and purchasers.* **Results** *The analytical tests have confirmed the consistent presence of asbestos fibers in DAS, about 30% in its composition. The documents found at the State Archive confirmed the annual purchase of several hundreds tons of raw asbestos from the Amiantifera di Balangero, the Italian asbestos mine. DAS was found to be used also within craftsmanship.* **Conclusions** *Asbestos fibers in DAS may have caused exposure to the manufacturer and a variety of users, including artists, teachers, artisans, and especially children. Over the 13 years of production, about 55 million packs have been produced and sold. The number of users is difficult to estimate but may have been in the order of millions. In Italy, a specific question on the use of DAS has been included in the questionnaire routinely used for interviewing mesothelioma patients. Information given in the present report may help to properly question mesothelioma patients about their past use of DAS as they may be unaware that DAS contained asbestos.*

INTRODUCTION

In public health, children should be given the most attention since they will form the future society. They should not suffer the consequences of exposure to pollutants during the most delicate phase of their life cycle. Prevention of exposure to hazardous agents should include attention to substances that may be present in toys[1]. For thirty years, regulatory measures on this issue have been focused on both materials and the way to use them. The first piece of legislation was issued in Italy in 1983[2]. This was followed by other acts, including a European Directive n. 378 in 1988[3]. Several studies have addressed the issue of safety in places of recreation[4–6]. Only some of these studies have detected opportunities for exposure to asbestos in childhood[7-9].

The present paper describes the use of asbestos in DAS which was widely used as a toy and teaching material in Italy and some European countries during the 60s and part of the 70s. "DAS", was a sort of artificial clay able to mold objects in various shapes and styles, which, unlike traditional clay, did not require baking to harden. Air drying makes the paste solid and stable with a hardness similar to that of conventional clays requiring treatment at high temperature. In addition to its use as a toy, other uses of DAS were in art laboratories and in conservation and refurbishment of pottery.

The presence of asbestos in DAS was first reported to our laboratory by a restorer of archeological pottery, who also provided us with an original box of the material(Photo 1, 2). DAS was produced and sold in powder and, later, as a wet ready-to-use paste(Photo 3).

For the purpose of this work, the presence of a significant quantity of asbestos was confirmed through qualitative polarized optical and scanning electron microscopy

(SEM). We integrated this observation with original administrative documents confirming the use of asbestos in DAS formula until 1975 and the quantities annually purchased. Finally, interviews with past employees were conducted, as they were the sole remaining source of information, in order to estimate the quantity of annual production, and to identify the most relevant suppliers and purchasers of the product.

METHODS

In order to describe in detail the history and composition of the mineral that characterizes this toy, statements were obtained from former past employees of the manufacturer: namely, the chief technician of the chemical laboratory and three administrative staff (two belonging to the export department and the third to the purchase department).

Purchase orders and sale invoices relative to DAS production were searched at the State Archives of Turin, where the original corporate documents of the seller are officially deposited and indexed.

Original samples of the toy, in powder and in paste, were also obtained and analyzed. The powder sample was that provided by the archeological restorer. The paste sample was recently bought on the web as a vintage toy. Subsequently, the period in which these items were produced was certified by the laboratory chief technician.

An original specimen of the ore of the Balangero asbestos mine (located in Northern Italy near the city of Turin) was used for the purpose of comparison.

The powdered DAS sample was first analyzed by Optical Microscope with polarized light with the technique of chromatic dispersion using Cargille liquids at different refraction index[10]. The same method was used to analyze the DAS in paste. Subsequently, the two samples were analyzed from the qualitative point of view by

SEM and X-ray Energy Dispersive (EDX) microanalysis, at the Department of Earth Sciences (University of Florence). The Balangero sample underwent the same SEM characterization[11].

Aliquots of the materials under investigation (powdered and paste samples, Balangero ore specimen) were placed on stubs using double-sided conductive adhesive tape, and subsequently coated by graphite. Secondary electron micrographs were obtained using a SEM ZEISS EVO MA15, by applying a potential of 20 KV to the electron beam. Subsequently, punctual and raster microanalytical investigations were carried out using the OXFORD INCA 250 microanalysis operating on the same SEM instrument.

RESULTS

Historical reconstruction of the DAS production

The firm Adica Pongo, which produced DAS, closed in 1993. The information on DAS preparation and formula was obtained through statements released by the chief laboratory technician formerly employed by the producer. According to this source, this product was invented in Milan (Italy) in 1962 by Mr Dario Sala (1912-2005), an eclectic person with inventive, creative, artistic and literary talent. He obtained a patent for his creation that he called "DAS", after his initials. He then ceded the patent for a pittance to a company, Adica Pongo, specialized in supplying school equipment, located in the province of Florence (Italy) that began a large-scale production of the toy. From 1962 to about 1965 DAS was produced and marketed, also as a toy for children, in powder contained in a cardboard box weighing 500 grams. In order to be used, the powder had to be mixed with a certain amount of water until obtaining a smooth paste. The dough could be molded for about three hours after preparation at room temperature. This was followed by complete drying and hardening at room temperature for about 24 hours. Towards the mid-60s the physical state of the product changed from dust to wet paste packed in plastic bags under vacuum in packs of 500 g and 1 kg, thus with no need for addition of water for molding. The container was in robust plastic film and the contents was kept under vacuum to avoid solidification. The composition of this artificial clay consisted of about 30 wt% talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, 30 wt% gypsum, $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$ and 30 wt% asbestos fiber, the remainder being a sort of glue, still covered by patent. The mineral fibers added to the product had the purpose of improving ductility and malleability as well as reinforcing the structure. Later, the percentage composition was changed and asbestos fiber content was reduced to about 25 wt%. Both the

statements and the traced purchase orders and sale invoices involving the asbestos mine (Amiantifera di Balangero – Turin, Italy) as the sole supplier of raw asbestos, indicate that the use of this mineral in the product lasted throughout 1975 and early 1976. From then until now the asbestos in DAS has been replaced with cellulose. Amiantifera di Balangero has been the biggest asbestos producer by quantity in Western Europe[12]. The original bills of sale / purchase issued respectively by the seller and the manufacturer, preserved by the State Archive in Turin, were recovered. In 1975, the last year in which asbestos was used. 17 bills refer to the purchase of about 30 tons each for a total amount of 510 tons of asbestos. In previous years, an annual average of about 800 tons of asbestos were purchased in order to annually produce about 2,650 tons of DAS.

DAS was initially sold only in the Italian market but after 1970, Adica Pongo organized an Export Department dedicated to trade with foreign countries. The main foreign purchaser of DAS was located in Netherlands. Other importers were in Germany, UK and Norway. In compliance with the increasing awareness of the risks caused by asbestos exposure, the British purchaser questioned the presence of asbestos in the product. Indeed, in 1974 the correspondence letters, still preserved in the Turin State Archive, give proof of the growing concern of the company about the danger of asbestos. In fact the General Management of Adica Pongo wrote to the company Amiantifera of Balangero asking about the possible presence of amphibole in their asbestos. Amiantifera replied on the 5th of July 1974, stating that “our asbestos is made up of pure chrysotile” and that “medical studies have shown that when asbestos is combined with other substances, such as in your case, it is deprived of the possibility to produce dust, thus excluding the risk of inhalation”. On July 8th, 1974, Adica Pongo required Amiantifera to produce the medical studies and

a written statement that their asbestos was totally amphibole free. Amiantifera refused to produce further qualitative analysis, and suggested the company refer to "the University of Florence for any qualitative determination of the asbestos fibers". Nevertheless, according to the purchase invoices, 510 tons of raw asbestos were still used during the whole of 1975 for the production of DAS and Amiantifera of Balangero still reserved 500 tons for the manufacturer but, according to documents, no more asbestos was purchased. Adica Pongo continued producing asbestos-free DAS until its closure in 1993. A further company took over the asbestos-free DAS formula in 1995, maintaining it under production until today.

Analyses of the material under investigation

The results of laboratory tests referred to the SEM investigations are shown in Table 1.

Table 1 - EDX microanalysis (averages more points of analysis) of the samples investigated. Results are expressed in wt%. Theoretical chrysotile chemical composition is shown, for comparison.

Element	Samples			
	DAS paste	DAS powder	Balangero	chrysotile**
<i>Mg</i>	24.9	21.4	24.8	26.3
<i>Al</i>	1.6	2.7	1.3	-
<i>Si</i>	21.5	22.5	23.4	20.3
<i>S</i>	2.0	2.9	< mdl	-
<i>Cl</i>	< mdl***	0.6	< mdl	-
<i>Ca</i>	2.1	3.2	< mdl	-
<i>Cr</i>	< mdl	1.2	< mdl	-
<i>Mn</i>	< mdl	1.7	< mdl	-
<i>Fe</i>	2.6	6.2	4.9	-
<i>O</i>	46.1	45.0	45.6	52.0
<i>Tot*</i>	100	100	100	-

* the values Tot wt% are normalized

** theoretical wt% evaluated from chrysotile ideal formula unit

*** minimum detection limit

The secondary electron micrographs of the DAS samples investigated are shown in Figures 1a-1d, showing the presence of fibers, grouped in bundles and elongated (Fig. 1a and 1d). The bending of the fibers (Fig. 1b and 1c) suggests the presence of chrysotile, $Mg_3Si_2O_5(OH)_4$. In the micrographs, obtained on both paste and powder DAS fragments, aggregates with predominant lamellar morphology consist of

gypsum and talc. Findings with SEM show no substantial differences between paste and powdered DAS with regard to presence and type of fibers. Figures 1e and 1f show the morphological characteristics of the Balangero chrysotile ore sample, used as reference (Fig 1e, 1f). Well curved fibers, peculiar characteristic of chrysotile, can be observed.

Table 1 shows the results of EDX microanalytical analysis conducted to verify the correctness of the attribution of the fiber fraction in the DAS to chrysotile asbestos.

The micro analytical results show a close similarity of the composition of the DAS samples with the chrysotile composition. Moreover, the average analyses of the two samples (paste and powdered DAS) are in good agreement with the analysis of the Balangero chrysotile. This result confirms the identification of fibers as chrysotile in the two samples of DAS. As far as the presence of minor elements is concerned, the two cases, toy and Balangero chrysotile, need to be discussed separately. Ca and S can be attributed to the presence of a certain amount of gypsum in the individual analytical points. Indeed, the dimensions in the excitation volume produced by the electron gun in the sample can involve not only the fibers but also grains or crystals of the other species, especially in this material, so intimately intermixed. Similarly, the occasional finding of Cr, Mn and Cl may derive from the species attached to the fibers. On the contrary, Al and Fe commonly occur as minor elements in chrysotile[13-14]. Thus, Al and Fe can be considered a good basis for the attribution of the origin of the fiber. In this case, the microanalytical content of these two elements agrees with the minor element composition of the fibers from Balangero, thus confirming purchase orders and sale invoices found at the State Archives in Turin.

Reconstruction of exposure

Between the early 60s and mid-70s, the composition of DAS included a substantial amount of asbestos. This may have led to exposure to asbestos of several categories of persons.

These include, in the first place, workers involved in the production of DAS, given that the raw material was used as loose fibers and the containers, firstly jute and later paper bags, arriving directly from the Balangero mine, were emptied into hoppers. In the workplace, there were no special dust control systems. For the users such as teachers, school children, artists, archaeologists etc, exposure to airborne fibers could occur before the addition of water and subsequently during finishing. Once hardened, in fact, the items were finished with either a chisel or abrasive paper, as suggested by the instructions on the box. Conversely, the same instructions did not take into account the risk of exposure.

The change of the physical state of DAS in paste deserves a specific consideration. On one hand, this transformation confined the exposure for the users to the finishing manipulation of the solidified items. On the other hand, this improvement did not affect entirely the production workers, who were still exposed to asbestos during the mixing process.

DISCUSSION

The results of the present study allowed us to determine without any doubt that asbestos was routinely used for DAS production during the 60s and mid 70s. Asbestos consisted exclusively of chrysotile fibers, provided during the relevant period by the Balangero mine. This material resulted in a peculiar source of exposure,

containing up to 25-30% by weight of asbestos. This value is more than twice that of asbestos-cement (around 13 wt%).

This finding leads to several considerations:

- for at least four years, DAS was marketed as a powder, thus easily polluting the indoor atmosphere where it was used,*
- the high percentage by weight of asbestos product has no equal in items mainly intended as toys;*
- the fact that children were an important target for the use of DAS is particularly disturbing, given their vulnerability to environmental hazards;*
- the total amount of asbestos used in about 13 years of production was around ten thousand tons out of the 35,000 tons of product. The number of packs sold is estimated to be in about six million of DAS powder and about 48 million of DAS paste. The number of end users is difficult to determine, but it may have been in an order of magnitude of some millions;*
- although the distribution was mainly in Italy, the product was certainly exported to the Netherlands, Germany, UK and Denmark.*
- in 1962, when DAS was invented and marketed, hazards of asbestos were already clear and widely reported in the scientific world[15-26]. Obviously, this was not the case of the inventor and (probably) of the producer of DAS, at least until 1974, when the British importer pointed out the problem.*

Molding was the major use of the product. The molded items, such as dried DAS, appear as a compact material, thus not able to easily release fibers into the atmosphere, unless they are mechanically disturbed with sanding or similar operations. The art crafts made of asbestos containing DAS did not, and do not nowadays, constitute any risk to people or the surrounding environment.

Nevertheless, they can still release fibers today if crushed or powdered, with consequent risk of exposure.

CONCLUSIONS

Incidentally a high percentage (25 – 30%) of asbestos fibres were detected by laboratory tests in a molding paste marketed in Italy between the midsixties and seventies. During this period several million packs have been sold, mainly in Italy but also in other European countries. Risk of exposure to asbestos fibres could occur to users, including children, because the product was also advertised and sold as a toy. In order to ascertain whether this exposure might have caused damage to the health of its users, this finding was first reported to the Italian mesothelioma epidemiological surveillance network, but it has never been the subject of scientific publication. Some previous reports of asbestos exposure among teachers and school children referred only to the presence of asbestos in place[27,28]. A limited presence of asbestos in toys has seldom been reported in the press and this issue has never been published in scientific journals. So apparently this work is, to date, the only one to report asbestos exposure as a consequence of the use of teaching materials during school time. Therefore, when interviewed nowadays, mesothelioma patients, and particularly teachers and ex-teachers, are questioned about the past use of DAS. The manipulation and in particular the finishing of items moulded with DAS in the 60s and 70s is interpreted as "certain exposure" to asbestos. The findings reported in the present paper suggest that enquiries about the use of DAS should also be made to mesothelioma patients in European countries other than Italy.

From the epidemiological point of view, it will only be possible to measure the dimension of the impact of this finding on the health of past users in a few years, when further information about the use of DAS will be collected from mesothelioma

cases where occupational, environmental or familial past exposures have not been tracked.

Figure 1 - Secondary electron micrographs of the investigated samples: a), b) DAS paste; c), d) DAS powder; e) and f) sample of Balangero chrysotile, for comparison

File: Electron Image_a

File: Electron Image_b

File: Electron Image_c

File: Electron Image_d

File: Electron Image_e

File: Electron Image_f

Photo 1 DAS powder in its original cardboard box

File: Das Photo 1

Photo 2 DAS paste in it's original vacuum plastic bag, ready to use

File : Das Photo 2

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File: Das Photo 3