From: Stephen Tan, Executive Director, PVC4Pipes, Brussels

To: European Chemicals Agency

CONTRIBUTION TO THE AGENCY CONSULTATION ON DIAZENE-1,2-DICARBOXAMIDE (C,C'-AZODI(FORMAMIDE), AZODICARBONAMIDE, ADCA) FROM PVC4PIPES.

1. **<u>Where is ADCA used in PVC pipe systems</u>**? – ADCA is used to create a rigid PVC foam in the core of a three-layer PVC pipe as show on figure 1a. The foam is shown in Figure 1b.

Figure 1a

Figure 1b.

The pipes are made by a co-extrusion process in which two streams of molten PVC 'sandwich' a third stream to which a small quantity of ADCA has been added. At the processing temperatures (typically ~200 °C) inside the extruder, the ADCA decomposes to form nitrogen, carbon monoxide and ammonia as shown below.

NH_2-CO-N=N-CO-NH_2 (ADCA) $\rightarrow$ N_2 + CO + NH_3 (1)
(Sant Prakash, W. Swam et alia J. Chem. Soc., Perkin Trans. 2, 1975, 46-50)

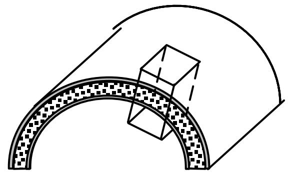
However, due to the high pressure inside the extruder barrel, the gases are dissolved in the polymer melt [(1,2).] When the polymer melt exits the die which is at the exit of the extruder, the rapid drop in pressure causes the gas to become supersaturated. Hence phase separation occurs and almost instantaneous nucleation of bubbles takes place. Bubbles will grow rapidly at first and then their growth rate decreases as the pressure within them diminishes. Bubble growth is also retarded as the polymer cools down and its viscosity increases. To prevent the foam structure from collapsing, it is essential to cool the material very rapidly. This is done by passing the foam through a chilled calibration unit so that the cellular structure is rapidly 'frozen' into place.

It is important to note that, in the process of making the foam core pipes, the decomposition of the ADCA into nitrogen, carbon monoxide and ammonia is essentially complete and that little or no ADCA remains in the finished pipe. This is demonstrated by the following analysis:

2. Analysis of foam pipes

- Several standard industrial pipe samples and also some foamed plates were provided by PVC pipe producer-members of PVC4Pipes. A reference foam profile sample made with a high level of foaming agent and purposely extruded so that the foaming process was incomplete (moderate extrusion temperature and low expansion of the foam) was supplied by SOLVIN laboratory in order to provide a sample where the residual ADCA-level would be higher than under standard industrial conditions.

- Structure of samples :
  the level of ADCA is measured with reference to
  the full sample (the foam layer + both solid layers when relevant).



The Solvay analysis protocol was the following : sample is dissolved in tetrahydrofuran (THF), the liquor is extracted by dimethylformamide (DMF). The final analysis of the DMF solution is carried out by HPLC. The result is compared with a blank and a standard mixture with known level of (non-decomposed) ADCA.

Result of the analysis carried out by SOLVAY Analytical department in May 2013

		Pipe A	foamed plate B	foamed plate C	foamed plate D	Pipe E	Pipe F	Pipe G	Lab profile foamed
Initial ADCA (*)	g/kg	Not known	0	1	2	Not known	Not known	Not known	3
Analysis of Residual ADCA	g/kg	< 0,01	< 0,01	0,02	0,02	< 0,01	< 0,01	0,02	0,06
Pipe diameter	mm	200	-	-	-	315	160	200	
Pipe / sheet thickness	mm	6.0	0.6	1.1	0.9	10.7	6.4	5.0	1.7
Remaining ADCA	% of initial			2%	1%				2%

Observations

The maximum residual ADCA was measured at ≤ 0.02 g/kg for the industrial foam core pipe samples. This confirms that the decomposition of ADCA during processing is essentially complete and that little or no residual ADCA is present in the finished foam core pipes.

It should be stressed that any remaining ADCA will be locked inside the polymer matrix of the foamed layer, which is itself encapsulated by the inner and outer solid layers of solid PVC.

3. **When were foam core pipes developed?** – processes for making foam core pipes was developed in the late 1980s, but they were not commercialised until the 1990s[3]. Even at this time, ADCA was the preferred foaming or 'blowing' agent. This is not surprising as an earlier patent[4] had described the use of ADCA for making foamed profiles. Since that time, cheaper, alternative blowing agents like sodium bicarbonate (SBC) have been evaluated, but have not been adopted, although current practice is to use a mixture of ADCA and SBC.

   OBSH (4, 4'-Oxybis(benzenesulfonylhdrazide) has been considered as an alternative chemical blowing agent; supercritical carbon dioxide has also been considered as physical blowing agent. However, neither proved suitable for making foam core pipes.

SBC is a well-established blowing agent because of its use as baking powder. Unlike the exothermic decomposition of ADCA, its decomposition is **endothermic** and reversible and takes place over a wide temperature range, which fortunately coincides with the processing window for rigid PVC foam. The decomposition products are CO_2, H_2O and Na_2CO_3 and the gas yield is 125ml/g, which compares poorly with the 220 ml/g of ADCA[5]. Compared with ADCA, its decomposition is slow and erratic [6].

ADC and SBC have complementary properties and exhibit synergism when used together. Their combined use has been reported to give better control of extrudate density, product colour, processability and cell structure [6,7].

4. **<u>What is the current European market size & value for these pipes?</u>** – the European market for foam core PVC pipes has grown to an estimated 400,000 tonnes per annum with a value of €400 to €500 million. This represents between 40 and 45% of the whole European market for PVC pipes. The major uses for PVC foam core pipes are in underground drainage and sewerage (D&S) and soil and waste (S&W) applications; the pipes have a predicted service life of at least 100 years [8].

5. **<u>What are the advantages of foam core pipes over alternatives</u>** – compared to solid-wall (compact) PVC pipes, foam-core pipes used between 25 and 35% less material in a pipe with equivalent stiffness. This is because the foam-core and solid inner and outer walls effectively constitute an I-beam, conferring stiffness on the structure[9]. PVC pipes in any case represent excellent conservation of resources, since PVC is derived only 43% from oil, the remaining 57% coming from naturally abundant salt (NaCl). Foam core pipes therefore represent an additional, valuable saving and have the added value that their light weight means that they can be readily handled manually on site without the need (in most cases) of mechanized lifting equipment. Life Cycle Analysis comparisons of foam core pipe with clay and concrete pipes used for D&S have shown significant advantages for foam core pipes, especially in the area of global warming [10]. Additionally, the foamed structure provides good acoustic damping and a lower thermal conductivity, which are valuable in S&W applications.

6. **<u>Why is ADCA used an how?</u>** - ADCA was chosen at the outset, due to the high gas yield on decomposition (220 ml/g) and the fact that the decomposition temperature can be 'tuned' through the use of 'kickers' to suit the extrusion process. Attempts to use sodium bicarbonate were unsuccessful, as the gas yield from SBC is much lower (125 ml/g) and decomposition is slow and erratic[6].

   ADCA is available from suppliers in a variety of physical forms; in the case of foam core pipes, the vast majority of PVC pipe producers use ADCA in non-dusting forms such as prills, tablets or granules. In many cases, the ADCA is fed directly to the throat of the extruder, being conveyed there from storage hoppers by pneumatics. Hence any possibility of exposure of process workers to ADCA dust is eliminated completely.

7. **<u>What is the fate of the ADCA that is added to the formulation?</u>** – as has been explained in Section 1, the whole idea of using ADCA as a blowing agent is that it decomposes during processing to form nitrogen, carbon monoxide and ammonia. Consequently, there will be little or no residual ADCA in the finished pipes and this has been confirmed by the analysis presented in Section 2. It should be stressed that any residual ADCA will be locked inside the polymer matrix of the foamed layer, which is itself encapsulated by the inner and outer solid layers of solid PVC. Consequently, there is no risk that users will be exposed to ADCA when they are handling (e.g. cutting) the foam core pipes when they are being installed and none at all once they are in service.

8. **<u>What alternatives for ADCA have been evaluated?</u>** – as stated above, the use of SBC has been extensively evaluated, since it is considerably lower cost than ADCA. However, the foam structures that result from using SBC alone are poor, with large and heterogeneous cell

sizes (Figure 3a) that lead to poor mechanical properties in the pipes. The foam structure can be optimised by the addition of ADCA, as shown in Figure 3b.

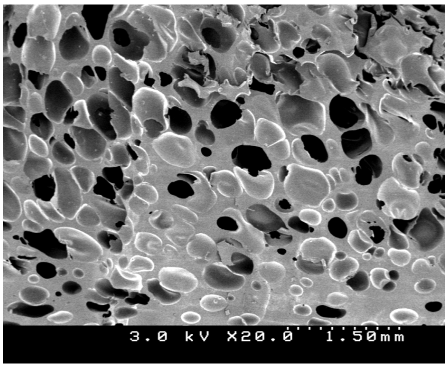


Fig. 3a – Structure using SBC alone(from 11)

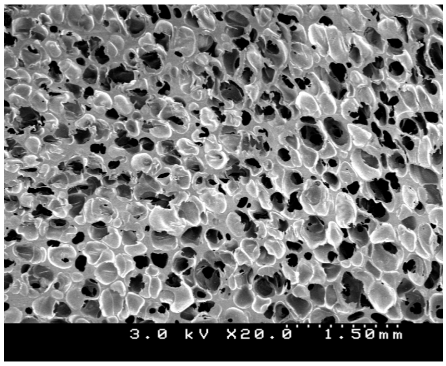


Fig. 3b – Structure using SBC + ADCA(from 11)

OBSH (4, 4'-Oxybis(benzenesulfonylhdrazide) has also been considered as an alternative chemical blowing agent, either on its own or in conjunction with ADCA(12); supercritical carbon dioxide has been considered as physical blowing agent(13,14,15). However, neither have proved suitable for making foam core pipes as the quality and consistency of the foams produced using these blowing agents are inadequate.

References

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