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To: European Chemicals Agency

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## **CONTRIBUTION TO THE AGENCY CONSULTATION ON DIAZENE-1,2-DICARBOXAMIDE (C,C'-AZODI(FORMAMIDE), AZODICARBONAMDE, ADCA) FROM INEOS CHLORVINYLs LIMITED**

We are writing to contribute details of our knowledge and experience of the above substance that has been used in our company for many years. The author also writes in a personal capacity as a contributory author to the publication *Handbook of Polymer Foams (1)* in the chapter that dealt in detail with the applications of ADCA and experience in the formulation development of numerous foamed products for specific applications in the flexible PVC industry.

INEOS Chlorvinyls is Europe's largest manufacture of pure PVC resins. These resins are sold to companies that mix them with a range of additives and process them to manufacture articles. INEOS Chlorvinyls does not manufacture ADCA nor does it use it as an ingredient in its products (it is fully aware, however, that it is used as a raw material by other INEOS businesses). INEOS Chlorvinyls does however have extensive experience of the formulation of PVC using ADCA and other foaming agents in order to understand the technical requirements of the PVC resins that it manufactures and how the foaming properties of these grades can be improved and developed. The aim of this document is to review the use of ADCA and other foaming agents and to demonstrate the importance of foaming in order to reduce weight, provide sealing, provide sound and thermal insulation, draught protection and to enable a variety of products meet exacting standards under a variety of legislative disciplines.

### 1. General Description of the areas of use

ADCA is used extensively in foamed flexible PVC. Its mode of action is to generate gas during the PVC melt phase. The melting of PVC occurs over a range of temperature, depending on the molecular weight, molecular weight distribution, the level of crystallinity of the PVC grade and the presence and level of additives employed. It is critical to tune both the level and particle size of ADCA - and whether further foaming accelerators are used - to the PVC resins and the remaining formulation ingredients. In order to achieve optimum foaming, both the temperature of ADCA decomposition and the rate of gas production influence

foaming and both the level of foaming (normally expressed as percentage expansion) and the “quality” of foam, as represented by the cells’ aspect ratio, which is normally measured by the size of cells and their type (open or closed). Such properties are critical to the successful production of the article. Whilst it is true that the flexible PVC foaming industry has developed its formulations around ADCA, it is not true to state that alternatives have not been evaluated. Some speciality products foam at lower temperatures with sulphohydrazide blowing agents but these remain a specialist application owing to requirement for very fast fusion to ensure that the PVC enters the melt at very low temperatures. Bicarbonate agents have also been employed but these do not give the same level of gas evolution and can rarely be used on their own. Further examples are given below.

## 2. Application Areas

In flexible PVC applications the critical applications of ADCA are found in the plastisol area.

PVC plastisols are mixtures of speciality grade PVC resins - often manufactured using emulsion polymerisation technologies - and liquid plasticisers and other formulation ingredients, including ADCA when required. The function of the plasticiser in such mixtures is two-fold: it imparts flexibility in the final product but it also provides the liquid phase of the liquid dispersion. Such liquid dispersions (see figure 1) can show various rheological characteristics such as Newtonian, dilatant or pseudoplastic. The great advantage of such systems is that they can be coated onto various substrates such as fibreglass, paper, metal, cloth or other plastics. These coated materials are then heat cured to first gel them together and then finally melt the polymer phase. If such plastisols contain ADCA, this will decompose when the polymer enters the melt phase, causing the melt to foam. For an even, controlled foam to result the PVC must be in the melt phase when the ADCA decomposes. This is the essence of ADCA use.

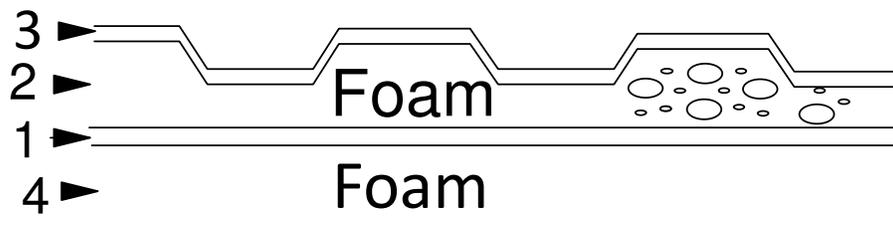


**Figure 1:** Typical PVC plastisol. The example shown has Newtonian flow characteristics but both dilatant (shear thickening) and pseudoplastic shear thinning) rheologies occur

The key product areas using ADCA are given below.

## 2.1. Flooring

PVC flooring is used both in contract (schools, hospitals, offices, hotels etc.) and domestic markets. Domestic applications produce the well-established cushion vinyl flooring product that generally contains both a foamed inner layer which is printed with relief inks and a foamed backing layer (which gives the cushion effect). Whilst the precise details of manufacture remain proprietary to the individual manufacturer there is a general mix of the order of laying down of each layer, although at some point all four layers will be melted to ensure full fusion and foaming agent decomposition.



**Figure 2:** Schematic of Cushion Vinyl Flooring showing an example of the order of layer manufacture (1 – Fibreglass encapsulation layer; 2 = chemical foam layer (inhibitible); 3 = clear wear layer; 4 = backing foam layer). In this assembly ADCA is used in layers 2 and 4.

Figure 2 shows a typical layout of a cushion vinyl flooring structure. It should be emphasised that each of these layers arise from a separate, distinctly formulated PVC plastisol. The plastisol will contain other ingredients such as thermal stabilisers, fillers and, for foamed applications, ADCA and any substances that work synergistically with it. The plastisol is spread, like paint, onto a surface, or sprayed or coated onto another substrate. In the case of cushion vinyl flooring, the first or base plastisol is coated onto fibreglass, with the plastisol saturating the porous glass. This saturated material is then solidified by heating, often on a hot metal gelling drum. Such a process solidifies the PVC but does not bring about the melting and full fusion of the polymer. Onto this solid layer a second plastisol can then be coated and this too is solidified. The same happens a third time with a clear PVC-plasticiser layer (the wear layer, the level upon which people will walk) and finally the whole assembly is turned over and a fourth, final, plastisol coated onto it. This becomes the backing layer, the layer which provides the foam.

Whatever the order of coating, when the whole assembly goes to a final fusion oven the PVC melts and the layers containing the ADCA foam release gas as the temperature reaches its decomposition temperature. Such ovens are often described as large pizza ovens and the similarity between the two processes can indeed be observed.

It should be stressed that:

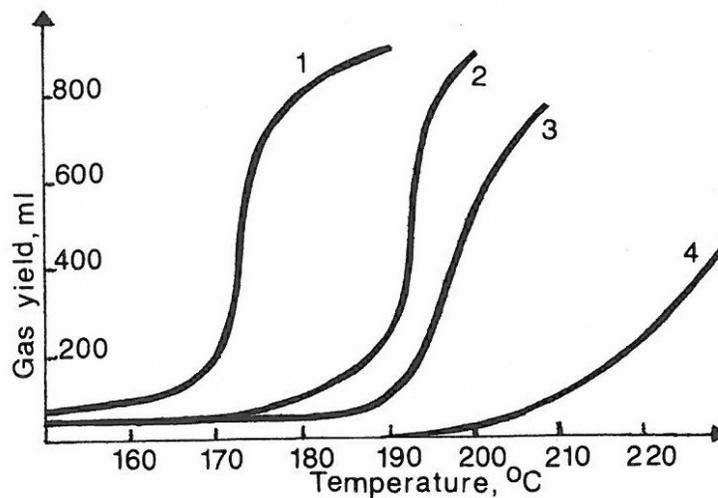
- (i) The ADCA decomposition and the melt viscosity of the polymer are linked and give the level of expansion.
- (ii) The steady gas generation – in correctly formulated products – gives the controlled expansion that result in the uniform foam that is required for the product. Too

rapid expansion in the backing foam layer results in surface defects that in turn mean that the floor cannot be laid flat; too rapid expansion in the internal/print foam layer can affect the interaction with the clear wear layer

- (iii) The foam characteristics of the printed foam layer must be carefully controlled. This layer is often printed with speciality inhibition inks that interact with the ADCA and prevent it decomposing. This results in a relief effect which means that where such inks were printed there is no expansion and where other, non-inhibited inks were used there is full expansion. This is the origin of the well-known tile effect, known as the Congoleum process (2), after the company that first developed and patented it. Full details were given in a publication by Niven (3).
- (iv) The expansion of the ADCA can be accelerated with Lewis Acids such as zinc oxide or retarded with substances such as benzotriazole or, in the case of water-based inks, thiourea derivatives. These add to the excellent versatility of ADCA for these processes.
- (v) Polymer resins are carefully selected for these applications so that the optimum viscosity of the polymer melt is obtained at the decomposition temperature of the ADCA. Any change in foaming agent therefore requires a complete change of the polymer system.

## 2.2. Synthetic Leather

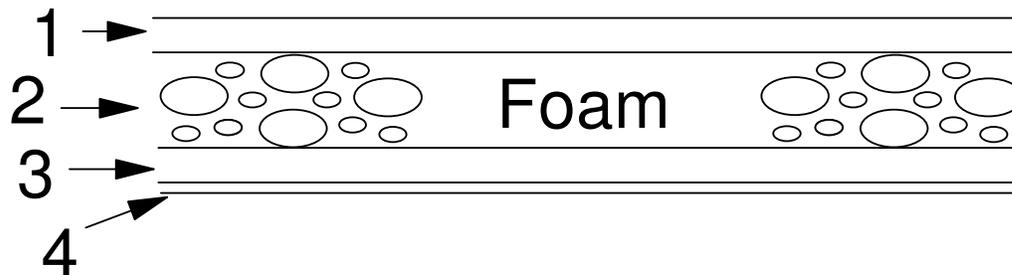
A significant industry has developed over the past fifty years for the manufacture of synthetic leather. Such products are used in a wide variety of applications. These include fashion products where the product competes with leather itself all the way to technically demanding applications such as automotive interiors. Such products, known as Unsupported Expanded Vinyl (UEV) are found around car dashboards, doors and seat covers and have a long list of technical requirements to fulfil in a highly tested and standardised area. Such products must (i) have sufficient strength so as not to collapse when vacuum formed at high temperatures into their respective panels (ii) have soft properties brought about by a combination of plasticiser level and foam level (iii) have even, smooth surfaces



**Figure 110** The effect of reactants on temperature of decomposition and yield of gas from azodicarbonamide: reaction medium 400 g dioctyl phthalate, 3 g azodicarbonamide; reactants: (1) 1 g zinc oxide; (2) 1 g zinc oxide, 0.25 g trimellitic anhydride; (3) no reactant; (4) 1.5 g thiourea

Fig 3: The effect of reactants on temperature of decomposition and yield of gas from ADCA: Reaction medium 400g dioctyl phthalate, 3g ADCA; reactants: (1) 1g zinc oxide (2) 1g zinc oxide, 0.25g trimellitic anhydride (3) no reactant (i.e. pure ADCA) (4) 1.5 g thiourea. Reproduced with permission from Reference 3

which are brought about by the optimum, gradual expansion of the foam, this being brought about in turn by the optimum decomposition of ADCA (iv) show high degree of tensile strength in use (v) show little or no emission of volatile ingredients so as to pass the most demanding automotive standards.



**Figure 3:** Schematic of synthetic layer: 1 = fabric, sometimes encapsulated, 2 = foam layer; 3 = top layer, 4 = rubber or silicone carrier for production

The molecular weight of automotive leather foams made in this way is higher than those made in the flooring industry so as to bring about both the high tensile strength requirements in the final product and to avoid collapse when the vacuum forming is taken place. This means that the onset of the decomposition of the ADCA, compared to that in the flooring applications, must be delayed and take place at a higher temperature since the higher molecular weight resin will have the optimum melt viscosity for foaming at a higher temperature. Once again the ability to bring this about comes from the extreme versatility of ADCA. Owing to its ability to have its decomposition activated by catalysts or retarded by deactivators ADCA gives the fabricator the ability to meet the most highly demanding standards required.

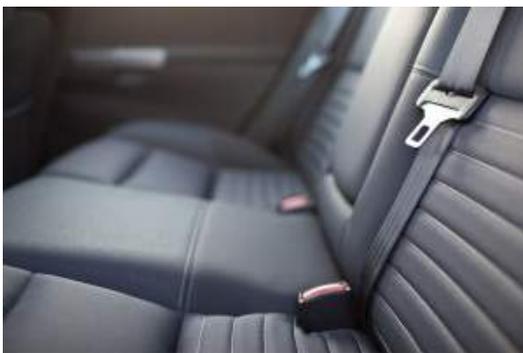
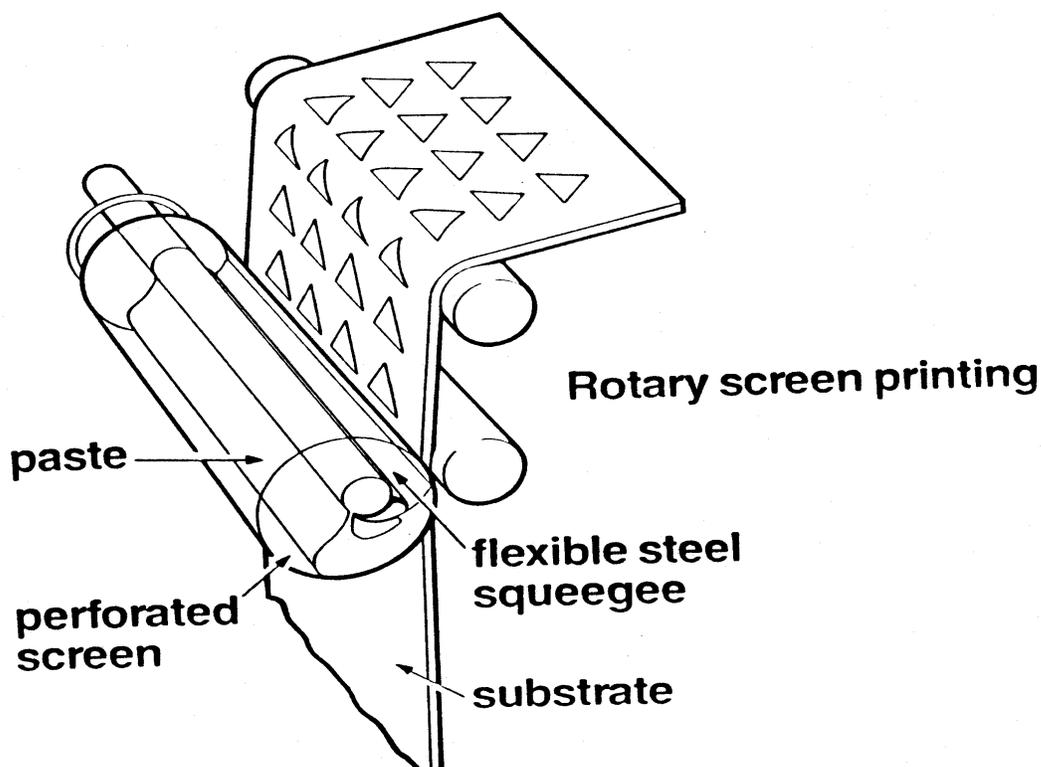


Figure 4: Example of automotive application of foamed vinyl

## 2.3. Wallcovering

ADCA has been an integral part of foamed vinyl wallcovering for decades. In a similar way to its mode of action with flooring and synthetic leather, ADCA functions in vinyl wallcovering by generating gas at the correct melt viscosity of the plastisol formulation so as to give a foamed and textured effect in the product. The advantage of vinyl-based plastisols is that owing to their liquid nature they can be printed in both a continuous coating but also can be applied via screen printing techniques in patterns so as to give a product which has areas of different relief (see figure 3).

One of the key aspects of such foamed products is their colour. The foams are predominantly white and manufacturers will generally manufacture to a whiteness



**Figure 5:** Screen printing of foamable vinyl plastisol/paste. In this design the plastisol is laid down in a triangular pattern and when fused these triangles will be foamed and have relief

specification as measured using a colorimeter, such as the Dr Lange LAB instrument. This measures the primary colours and expresses the degree of yellowness as a yellowness index. A prime cause of yellowness in such products is the presence of undecomposed ADCA. A typical value for a specification is 0.5 Yellowness Units. Such a value is generally taken as being the point at which yellowness can be detected by the human eye. Such values indicate that the levels of residual ADCA in these products is exceedingly low and current work aimed at calibrating YI with residual ADCA is underway.

### 3. Insulation and protection foams

Flexible PVC foams may also be used to give padding and protection. These are differentiated from flooring, synthetic leather and wallcovering foams by the level of expansion. They contain significantly higher quantities of ADCA so as to bring about exceedingly soft foams that can be used in a variety of important applications, although since the product relies on complete decomposition they will not contain higher quantities of residual ADCA. These include draught excluders and glass protection foams. These must be easily deformed but have the ability to return to their original thickness when the load is removed, i.e. they must have high resilience. These foams are based on ADCA.

### 4. Fundamentals of ADCA decomposition: relationship with PVC Melt Rheology

#### 4.1. Chemical foaming agents

The gelation and fusion of foamed PVC by heat involves a number of different processes, each of which is required to produce a product of the desired properties that has sufficient tensile strength in the shape and conformation desired, e.g. profile, moulded article, flooring, wallcovering. In such a thermal process, the PVC resin is heated:-

- (i) First from room temperature to a temperature above its *glass transition temperature,  $T_g$* . This is the temperature at which polymer chain-chain interactions are lost and polymer chains can now flow past each other easily. To the observer this is observed by the transformation of PVC from a glass to a rubber.
- (ii) Above  $T_g$  the PVC chains are gradually melted and a homogenous mix of all formulation ingredients, including ADCA as the polymer enters the melt.

- (iii) Full melting occurs, as evidenced by a reduction in the viscosity value of the polymer formulation, as measured by dynamic viscometry (see Figure 4).
- (iv) When the temperature of ADCA decomposition is reached, the ADCA decomposes, evolving gas that expands the polymer melt.
- (v) When the polymer leaves the oven or extruder, it cools down to room temperature. In plasticised formulations the plasticiser will now be interacting with polymer chains and PVC-plasticiser interactions will have replaced many of the PVC-PVC interactions

The amount of expansion in such a system depends upon several factors:

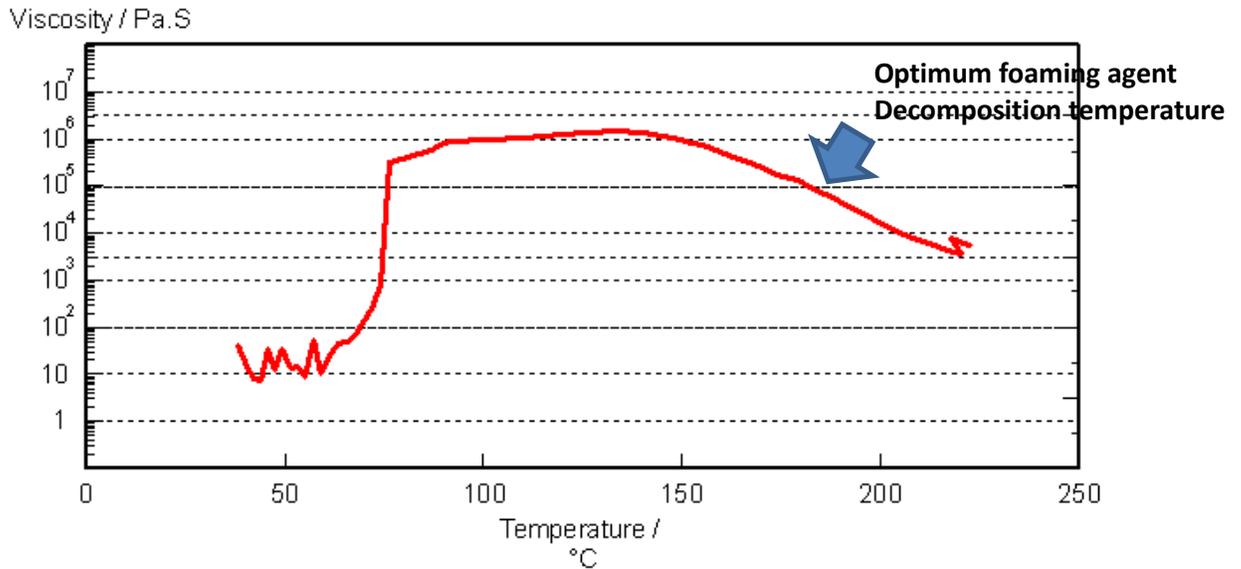
- (i) The level of ADCA has a profound effect: more ADCA results in more gas generation and more expansion. Thinner coatings are easier to expand since the temperature profile across the coating is more even than the profile across thicker coatings.
- (ii) The particle size of the ADCA also has an effect: the smaller the particle the more rapid the decomposition and expansion. ADCA manufacturers will tailor particle size for different applications
- (iii) The presence or absence of an activator or inhibitor. As described above, the decomposition of the ADCA can be speeded up or retarded. Such catalysis can reduce the temperature at which the ADCA decomposes. In many cases this is essential since polymer degradation can often occur before the true decomposition temperature of pure ADACA is reached. This ability to tailor ADCA decomposing to different circumstances is one of the great advantages of the ADCA-system and one that is not present in alternatives.
- (iv) The level of plasticiser has a direct effect on the viscosity of the melt. Greater plasticiser levels, with other variable remaining constant, reduces the melt viscosity and hence increases the level of expansion
- (v) Similarly polymer molecular weight has a major influence on the level of expansion: high molecular weight resins give higher melt viscosities and hence lower expansion. The selection of polymer for the foaming process is of great importance: not only does its molecular weight and molecular weight distribution directly affect melt viscosity but the surface tension of the polymer at the ADCA decomposition temperature has a direct effect on the size of gas bubbles. In general the expansion of gas bubbles follows the Laplace equation but the surface tension of the polymer particles, which will contain a surface of

surfactant, also has a critical effect on the size of the bubbles and the thickness of the cell walls of the foam bubbles.

The events described in parts (i) to (v) above are shown in Figure 6.

A full description of these events is given in a paper by Boscott and Coulson (3,4) and Birch (5). The maintenance of the appropriate foaming conditions during manufacture is critical: small changes in melt viscosity or production speeds can bring about unacceptable deterioration of foam quality, both in terms of the amount for foaming but also texturing at the foam surface. Figure 5 shows the physical consequence of ADCA decomposition before the optimum melt viscosity is reached. The expanding gas experiences far high resistance in the higher viscosity melt and fine gas bubbles coalesce to form larger ones. These eventually reach the surface and cause a dramatic rupturing of the surface. Since foams are generally required to sit flat on a surface or tight against a barrier, such as those for draught excluder foams, such surface defects are totally unacceptable. Since such disastrous effects are seen by such a small deviation with ADCA, a change to an alternative foaming agent which decomposes at significantly different temperatures still will increase the magnitude of these disastrous effects.

It should be mentioned that in some cases the production of such textured surface is intentional. This is seen in a niche wallcovering sector which produces textured foam as a fashion design. Whilst details of such foam formulations remain proprietary information to the producer, it is known that the foams are produced by the intentional early decomposition of foaming agents. However in this application the effect is purely cosmetic: the product will not sell to demanding technical specifications that are seen in other areas (see below). These sulphahydrazide foaming agents, however, are one of the few known alternatives to ADCA and the effect of such a change can be seen as dramatic.



**Figure 6:** PVC Melt viscosity curve as measured by dynamic mechanical rheometry. ADCA in such formulations will decompose in the 175°C to 185°C region, depending upon application and foam activator (“kicker”) employed. Note that the Y axis is on a logarithmic scale: the viscosity difference between 150 °C and 175°C is ca. 900,000 Pa.S. Decomposition of ADCA at 150 °C results in very little expansion and often surface blistering owing to excess melt viscosity (see Figure 7, foam A): decomposition at 200 °C will completely destroy the surface since the melt viscosity is too low (see Figure 8, Foam B). Hence the critical nature of the tuning of expansion to melt conditions is shown.



A

B

**Figure 7:** Effect of ADCA decomposition below the optimum melt viscosity (A), with standard conditions (B), all other parameters being equal. The foams also show differences in compression recovery



A

B

**Figure 8:** Further evidence of the critical effect of formulation on the properties of the final foam. Foam A is a side view of Foam B in Figure 5; Foam B is one in which the ADCA has decomposed after the optimum melt viscosity has been reached. Note that the level of overall expansion is the same but the foam properties are distinctly different, with foam B failing all standard foam property tests (indentation resistance, indentation recovery, water absorption, colour and general aesthetic properties)

## 4.2. Mechanical Foaming Agents

Mechanical foaming is not unknown in this area and deserves to be studied as an alternative *process* for the production of foamed flexible PVC articles.

Production of mechanically foamed flexible PVC can be made by incorporating air, under pressure, into a vessel of PVC plastisol as it is stirred. The foamed, aerated plastisol can then be stabilised by the addition of surfactants and then immediately spread onto the relevant substrate for the production of articles. Work has been performed in industry to optimise such formulations in terms of foam density. Such foams can be cheaper in cost owing to the absence of chemical foaming agents but can suffer from a difficulty to obtain very low densities (there is a physical limit to air pressure and highly aerated foams are often prone to collapse in the wet state whereas for chemical foams lower densities simply require higher levels of foaming agent). Additionally since the first result of heating an aerated plastisol is to reduce its viscosity there is a danger that the wet foam density can be lost before the plastisol reaches the gel state. This can be overcome by the use of fast solvating plasticisers, traditionally butyl benzyl phthalate but more recently low molecular weight benzoate esters, but these are only partially successful in producing foams of similar density to low density chemical foams.

However the other practical aspect is that mechanical foams generally result in dry foams of an open cell nature. This makes the production of resilient foams (see below) impossible and such technologies have generally not been favoured in products that have technically demanding foam requirements.

## 5. Further technical considerations: quality and standards

Whilst significant areas of the flooring and wallcovering applications are sold on their design features into domestic markets, significant amounts of foamed goods are also sold to strict product standards into applications such as schools, hospitals, offices and local authority housing. In these the products must comply with strict product standards that effect resilience of foamed articles (resistance to, and recovery from, indentation), sound deadening and thermal insulation are also important properties. A non-exhaustive list of such standards is given below:

## 5.1. Flooring

Key products standards involved are EN 433 (Determination of residual indentation after static loading), EN424 (Determination of the effect of the simulated movement of a furniture leg) and EN425 (Resilient and Laminate Floor coverings, Castor Chair test). These standards relate to the level of indentation that is shown by the floorcoverings under the load and also the speed of recovery of the foam when the load is removed. This simulates such events as the moving of a bed in a hospital or table in a school where it is important that an indentation disappears as soon as possible. This property is directly related to the foam structure which in turn depends on the proper expansion of the foam caused by the efficient decomposition of the ADCA.

Other important characteristics driven by foam properties are the sound insulation properties. This is an important feature of flooring with foamed backings both in houses but particularly in public housing projects and apartment blocks in which sound deadening is provided by the choice of flooring material. Some local authorities specify sound deadening from the construction materials of apartment blocks but in other authorities this is done by specifying foam-backed PVC flooring which has an acoustic specification. The sound deadening properties of the foam layers comes from the quality, density and expansion level of foam layer, all of which depend upon the use of ADCA and the expansion properties described above.

## 5.2. Unsupported foams

These are the types of foam that are used in draught exclusion and glazing protection applications. Product standards such as EN ISO 3386-1 (Polymeric materials, cellular flexible – Determination of stress-strain characteristics in compression – Part 1: Low-density materials) specify the foam characteristic properties that are required in such products. There is an essential requirement for the cells to be of the closed cell type for such materials to ensure that the foam provides a barrier to draughts and also provides adequate cushioning of the window or doors. The method of obtaining 100% closed cell foams for such applications is well understood and a key requirement is the use of ADCA.

## 5.3. Automotive leather

As indicated above, Unsupported Expanded Vinyl (UEV) is manufactured from plastisol-based PVC resins which are foamed using ADCA. Traditional synthetic leather (see Figure 2)

coats plastisols onto a fabric backing but the advantage of using vinyl without the fabric backing is that it reduces the overall weight of the final product - a particularly importance factor for modern automotive assembly. Weight savings of 20 to 25% are commonplace. However in order for the vinyl to have sufficient strength – strength is normally given by the fabric backing - it has to be made with resin of higher than average molecular weight and these are employed with specialty formulation ingredients. In order for these resins to be foamed the decomposition of the ADCA needs to be delayed until higher than average temperatures are reached. This technology has been developed and it has been developed around ADCA. This means that when vacuum-formed around door panels and dashboards, the vinyl has sufficient strength to be moulded without the foam collapsing. Automotive companies will have their own additional requirements that will be reflected in internal product standards. An example is the General Motors standard GM BOCTM 31-152. A typical failed test specimen for vacuum forming tests is shown in Figure 9:



Figure 9: Vacuum formed foam sample for UEV tests: foam around base shows effect of uneven expansion or “Elephant Skin” effect. Sample received just 10 seconds over expansion in the processing oven, illustrating the Sensitivity of the foaming process. Foaming agent = ADCA

## 5.4. Rigid PVC Foams

These products are distinctly different from the ones described above, but no less important. Since rigid, i.e. non-plasticised, contains no plasticiser it has a greater density than its plasticised counterpart. This is because the density of PVC resin is 1.4 kg per cubic metre and that of common plasticisers is just below 1 kg per cubic metre. Therefore the use of plasticisers reduces the density of PVC articles. Since these components are not present in rigid PVC other methods of weight reduction can be used whilst not giving rise to flexibility. One way to do this is to foam the PVC article and such products – foamed profiles and foamed PVC pipes – have significant markets. The great property of these is weight reduction in construction products. Plastics already have far lower weights than metallic or concrete products and further light weighting takes this further.

### 5.4.1. Background

The first products based on rigid PVC foam were manufactured in the early 1970's (7). Since then there has been a steady increase in the use of foamed vinyl in both Europe and the USA. Demand in recent years has grown because of improvements in processing equipment, developments in formulation technology and a constant drive towards novel applications.

There are numerous benefits to using foamed products (8,9): they provide lower cost per unit volume, higher stiffness for a given weight, ease of fabrication and machining, lower thermal conductivity, lower coefficient of thermal expansion, good acoustic damping properties and improved resistance to wind-load.

Many of the applications for rigid PVC foam profile are for wood-replacement products. It can be sawn, nailed or screwed, thus allowing use of wood-working methods. Foamed extrudates can be produced to resemble wood in terms of structure, appearance and colour. The substitution of wood by foamed vinyl is being driven by the advantages of a maintenance-free product (9), the rising price of lumber and environmental pressure to protect forests. Other benefits of PVC foam over wood (9, 10, 11) include chemical resistance, good weatherability, good fire retardancy (Class B1 based on DIN 4102) and resistance to vermin. The main obstacles to its use are its reduced toughness and higher cost. However, although PVC foam is more expensive than wood on a cost/volume basis, it can be extruded into complex shapes without the finishing operations and scrap associated with the manufacture of wood trim.

## 5.4.2. Rigid foam formulations

PVC foam profile is used in both interior and exterior applications. Some examples of the former are skirting boards, cornices, wall and ceiling panelling, curtain rails, guide rails for shutters, coving and furniture profiles. Examples of the latter include cladding, soffit boards, roofing products, window-sills and door-frames.

In order to produce a structure with the minimum weight for the required stiffness and impact performance, it is important to control the foam density, skin thickness, surface finish and cell size distribution. This can be achieved, firstly, through the choice of processing equipment (11, 12), secondly, through the choice of processing conditions (13, 14), and, thirdly, through the choice of formulation (15).

As with foamed flexible PVC products, there is a complex formulation technology involved in the production of rigid PVC foam products. Formulations contain a mixture of processing aid, thermal stabilisers, lubricants, pigment and filler in addition to the blowing agents required to produce the foamed structure. The type of PVC resin and other ingredients in the formulation control the powder flow, gelation behaviour, thermal stability, melt rheology and melt strength of the material during the production process, and obviously have a profound effect over the properties of the end-product.

Rigid PVC foam is processed from a dry blend (a dry mixture of all formulation ingredients that has been taken above the glass transition temperature of the polymer but not melted) on parallel or conical, contra-rotating, twin-screw extruders. As with flexible PVC, the cellular structure is produced by the decomposition of chemical foaming agents. The gaseous decomposition products are generated within the extruder barrel and dissolve in the molten polymer (16, 17). Dissolution is possible because of the high melt pressure within the extruder. To achieve an optimum foaming operation it is essential that bubble nucleation is delayed until the polymer melt emerges from the die.

When the polymer melt exits the die, 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.

Many aspects of the foam morphology are controlled by the formulation. Cell size and uniformity depend critically on the amount and type of chemical blowing agent: a uniform, closed, fine cell structure is desirable for most applications. Cell size is also a function of the rheological properties of the polymer, as is seen with flexible PVC foams. If the polymer viscosity is too high, then the bubbles will not be able to expand fully, and it will not be possible to achieve a low density foam. If the polymer viscosity and melt strength are too low, the cells will rupture and/or collapse. In the case of PVC, melt strength is determined by the molecular weight of the polymer and by the use of acrylic processing aids. Hence both blowing agent and processing aid are key ingredients in the formulation.

#### 5.4.3. Foaming agents for rigid PVC foam

The two main foaming agents used in the production of rigid PVC foam are azodicarbonamide (ADC) and sodium bicarbonate (SBC).

As with flexible PVC foams, the relative amounts of the ADCA decomposition products formed depends on the decomposition mechanism of ADC, which varies as a function of environmental factors, such as pH (18). Although the decomposition temperature of ADC lies outside the processing window of rigid PVC foam, there are numerous activators or kickers (19) that can lower the decomposition temperature into the required range. Some examples of these are the same zinc salts that are used in flexible PVC foams, which are also added as thermal stabilisers for PVC (20). A blowing agent that is sometimes mixed with ADC to act as a kicker is Oxybisbenzenesulphonyl hydrazide (OBSH) (21).

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<sub>2</sub>, H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub> and the gas yield is 125ml/g, which compares poorly with the 220 ml/g of ADCA. Compared with ADCA, its decomposition is slow and erratic (22).

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 (22, 23).

Thomas and Harvey (24) showed that the optimum combinations of ADCA and SBC in the same formulation can be found. They showed using some elegant statistically designed experiments where the optimum combination of the two foaming agents lay across several foam properties – melt pressure, torque and foam density. The study found that, as expected, the level and type of blowing agent had the dominant effect on foam morphology. Cell diameters in this foamed sample are typically in the range of 300 - 700 $\mu$ m. Other formulations containing SBC at different levels but without ADC were also found to have cell diameters in this range, irrespective of the processing aid level and type, or type of filler used. Figure 9 shows a Scanning Electron Micrograph (SEM) of the resulting foam.

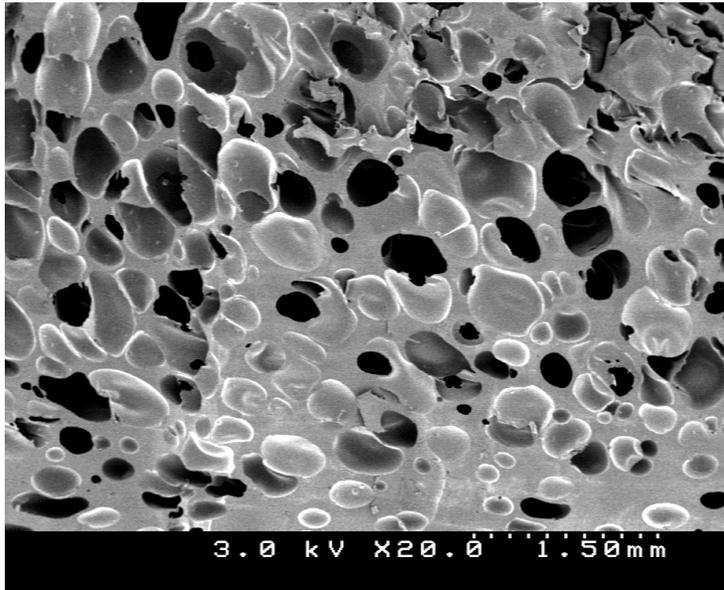


Figure 9: Rigid foam structure with SBC as the only foaming agent (SEM)

Addition of ADC gave a dramatic reduction in cell size. Figure 10 shows the cell structure of a foam sample which contained a mix of both foaming agents.. It seems that nitrogen bubbles from the decomposition of ADC act as nucleation sites for bubbles of CO<sub>2</sub> from the decomposition of SBC. The average cell diameter is now about 100  $\mu$ m. further work allows this combination to be optimised (Figure 11).

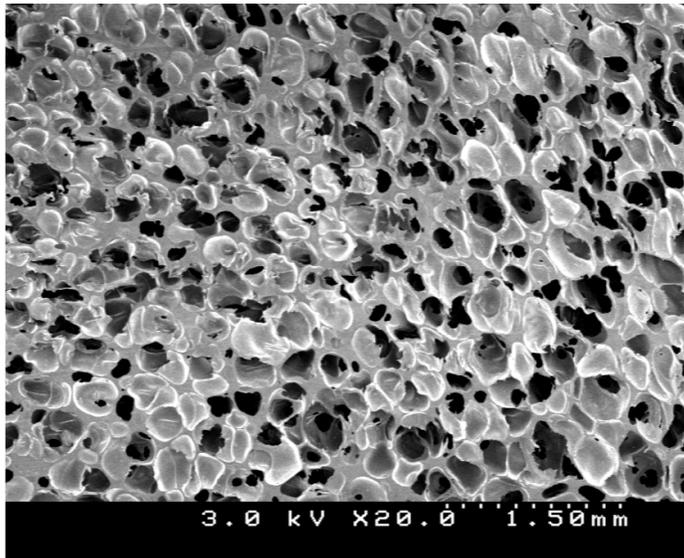


Figure 10: Effect of introduction of ADCA to foam in figure 9

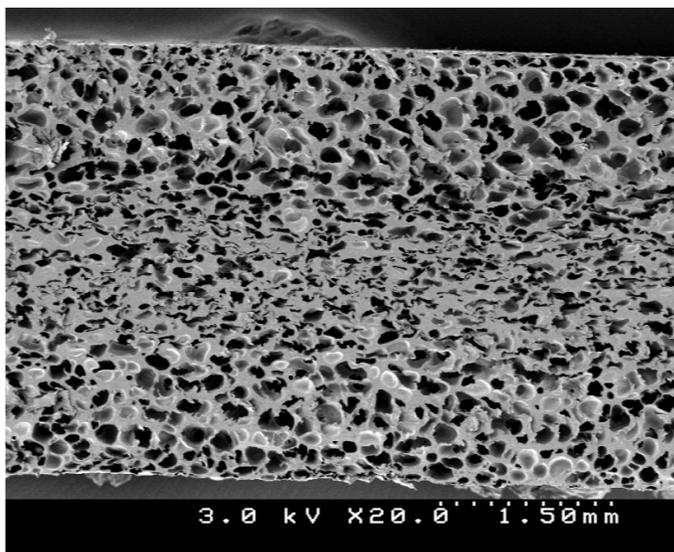


Figure 11: Intermediate (optimised) foam structure

A simple, empirical quadratic equation was fitted to these data to describe the relationship between foam density and the formulation variables. It was found that foam density decreased with increasing addition levels of blowing agents, reached a minimum and then started to increase again as blowing agent levels continued to rise. This phenomenon is due to cell collapse. The study showed that it is essential to use both ADCA and SBC in such products to obtain the optimised product.

## 6. Conclusions and summary

INEOS Chlorvinyls does not manufacture or sell ADCA but has decades experience of working with formulations containing it. It recognises the importance of the substance and the extreme difficulty in the identification of viable alternatives. Alternative substances have been evaluated but decomposition temperatures and rates of gas evolution make their use on their own in flexible PVC systems unable to meet exacting product standards. Owing to its manufacture and use of hazardous substances INEOS Chlorvinyls keeps extensive occupational hygiene records and has no record of the induction of occupational asthma from the use of ADCA in its research and development laboratories. Given that the substance can be used in non-dusting, compounded or pasted forms, it can be used without the hazard – respiratory sensitisation of the pure powder – being encountered. Indeed, this seems to be a sensible outcome and we think it more appropriate that the substance be referred to the restriction rather than the authorisation process.

ADCA is one of the most expensive components of a foamed PVC formulation. It is not used because of any low cost characteristics and alternative products that are far cheaper, such as sodium bicarbonate, foam at different temperatures and with less gas evolution so that there is no match of melt viscosity with the gas generation when used alone. The effect of using sodium bicarbonate alone is similar to using it alone, without yeast, in bread making: less expansion and only used for certain speciality products.

The level of expansion in expanded vinyl depends upon several factors. One of the most important is to ensure that gas expansion occurs when the melt viscosity and melt strength of the vinyl formulation are correct so as to ensure the correct level of expansion and the optimum cell structure. Very small changes in temperature cause dramatic changes in melt viscosity and melt strength, causing loss of foam properties, since the viscosity of the polymer melt can change dramatically with just a few degrees of temperature change.

These adverse properties include surface disruption, poor cell structure and collapse of foam.

The science behind the foaming of these products is well researched and well understood.

Foamed PVC products are sold according to several demanding specifications. Only slight changes in foam characteristics will mean that such standards will not be able to be met, as is evidenced by the observations that a change in activator for ADCA makes the foam properties inferior: changing to a different foaming agent completely is worse. Loss of ADCA will result in enormous disruption to the supply of these products and since the ADCA can be used safely this seems to serve no purpose.

We would be happy to discuss these issues further.

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## Note on the author

Dr Chris Howick took his BSc degree in Chemistry from the City University, London, UK and his PhD in Chemistry from the University of Nottingham, UK. He joined ICI in 1989 and worked on a series of research projects on PVC additives, particularly on the development of low migration plasticisers for food packaging applications. His studies into the fundamental aspects of plasticisation and flexible PVC resulted in him co-authoring the Plasticisers chapters for the Ullman's Encyclopaedia of Industrial Chemistry in 1990 and the Kirk Othmer Encyclopaedia of Chemical technology in 1991. The work also resulted in a co-authored paper in *Polymer* that was one of the first examples of solid state NMR spectra of flexible PVC. He then wrote the Plasticiser chapter of Professor Geoffrey Pritchard's *Plastics Additives* reference book in 1998.

Dr Howick joined the European Vinyls Corporation where he worked on variations of emulsion PVC for the development of new PVC resins for the flexible PVC sector (which were covered in the Royal Society of Chemistry *Green Chemistry* journal). This included fundamental work on foamable PVC plastisols for the flooring, wallcovering and synthetic leather industries. He wrote the flexible PVC foams Chapter of the POLYMER FOAMS textbook, edited by David Eaves of RAPRA Technology, in 2004.

Since 2006 Dr Howick has worked on REACH registrations and evaluations.