ICOD ASSOCIATES

AZO Presentation

David M. Henshaw

Anthony G. Martin

20 Blowing Agents

J. H. EXELBY and R. R. PURI
Schering Berlin Polymer Additives Group

D. M. HENSHAW
Witco Corporation

20.1 INTRODUCTION

The advantages of foamed or expanded products are numerous and depend on the application. In rigid products, weight reduction can be a benefit in terms of economics and for technical reasons such as improved insulation, machinability, and avoidance of sink marks in thick-walled sections. In flexible products, foams are produced for their greater comfort in terms of softness, warmth, and resilience, for the opportunity they provide in producing a surface texture for decorative

effects, for their ability to seal against irregular surfaces, for use in flotation equipment, for thermal and sound insulation, and for the chance to achieve material cost savings.

Production of foams is seldom straightforward, however, and requires considerable expertise from both the formulator and the processor.

The earliest production of foamed PVC can be traced back to the late 1950s and early 1960s. At this time there were already several methods available from other technologies for producing foams, namely by physical, mechanical, and chemical means. Another distinction worth making is whether the foam is produced at elevated or atmospheric pressure.

Physical foaming processes rely on the use of physical blowing agents. In these processes a change of state from liquid to gas occurs as a result of a heating process or by release of pressure. This change is endothermic, which can be helpful in avoiding excessive heat buildup in articles having thick cross sections. The use of physical foaming methods for the production of polyvinyl chloride (PVC) articles has not been commercialized to any large degree, and an example illustrates the difficulties associated with these processes. In the so-called elastomer process for PVC, a plastisol is pumped at 30 atmospheres pressure and is mixed with CO_2 at similar pressures in a cooled reactor tube (1). Specialized equipment is needed, and this has limited the development of these types of processes.

The same problem applies to mechanical foams. These are produced using special pumps which mix air with a plastisol, and the resulting foam is stabilized by special surfactants in the plastisol. The foam is then spread and fused. There are other limitations with this system which are discussed more fully in Section 20.10.

Most widely used in PVC is the production of foams using chemical blowing agents; these can be defined as compounds which are thermally unstable and decompose to yield gas at the desired polymer processing temperature. A very large number of chemical blowing agents have been proposed over the years, but few have survived to the present day. Listing the attributes of the ideal blowing agent helps explain why this is so (2).

- Gas should be evolved over a definite and narrow temperature range which is the same as the desired polymer processing temperature.
- Rate of gas release should be controllable but rapid.
- The blowing agent and its decomposition residues should be nontoxic.
- The blowing agent should have good storage stability.
- The product must be cost-effective.
- The blowing agent should disperse readily in the polymer.
- The residues should be colorless, nonstaining, and odorless.
- The gases produced should not be corrosive, and therefore nitrogen is preferred.
- At decomposition a large exotherm is undesirable.
- The blowing agent and its residues should not affect the thermal stability or processing characteristics of the polymer.

The first chemical blowing agents were used in rubber during the last century. These were generally inorganic carbonates, which suffer from (a) poor dispersibility in the polymer mix and (b) gas evolution which is not easily controlled, giving rise to foams with an open and coarse cell structure. The advantages of organic blowing agents started to emerge with the introduction of diazoaminobenzene (DAB) in 1940; again the first use was in rubber, and the advantage of this compound was the ability to form closed cell foams with conventional processing equipment.

Pronounced staining of articles in contact with foams produced using DAB limited its suitability (3), but further development of azo compounds resulted in widespread use of 2,2'-azobis-isobutyronitrile (AIBN) in PVC in the early 1940s. Toxicity of the decomposition residues caused

this compound to fall from favor, and thus the stage was set for the entrance of azodicarbonamide (AC or azo, but also known as ADA, ADC, or ABFA).

AC fits most of the conditions listed in the foregoing, but appears at first to have too high a decomposition point to be of use in PVC. However, discovery in the late 1950s that AC decomposition is reduced by the same metal compounds used to stabilize PVC has resulted today in its dominance of the PVC market. Accordingly, major attention in this chapter is focused on AC.

The only other class of compounds to find significant use as blowing agents in PVC today are the sulfonhydrazides, in particular p, p'-oxybis(benzenesulfonhydrazide) (OB), which is used in small-volume specialized applications.

20.2 MAJOR SUPPLIERS OF PVC BLOWING AGENTS

The major suppliers of exothermic blowing agents to the U.S. PVC processing industry are shown in Table 20.1.

20.3 PROPERTIES OF BLOWING AGENTS

Physical properties of the blowing agents azodicarbonamide and p,p'-oxybis(benzenesulfonhydrazide) are shown in Table 20.2.

20.4 DECOMPOSITION REACTIONS

Azodicarbonamide The reactions involved in the thermal decomposition of azodicarbonamide are complex and depend upon the heating rate and the environment in which the decomposition occurs—for example neat AC, or AC in a PVC compound in the presence or absence of an activator (Section 20.6), etc.

As shown in Figure 20.1, it is believed that primary decomposition of azodicarbonamide takes place by reactions 1 and 2, with a secondary reaction 3 taking place as isocyanic acid (HNCO) becomes available. Isocyanic acid can take part in other secondary reactions to give solid decomposition products as shown in reactions 4 and 5, or it can react with traces of moisture to give carbon dioxide and ammonia as shown in reaction 6.

Other decomposition mechanisms have been proposed leading to the production of biuret ($H_2NCONHCONH_2$) as a component of the solid residues.

TABLE 20.1 Major Suppliers of PVC Blowing Agents in the United States[a]

Company	Registered trade name	Products		Manufacturing location
		AC	OB	
Dong Jin Chemical Industries Co., Ltd	Unicell	×	×	South Korea
Miles (Bayer)	Porofor	×		Germany
Otsuka Chemical Co., Ltd.	Unifoam	×		Japan
Schering Berlin Polymers Additives Group[b]	Ficel	×	×[c]	United Kingdom
Uniroyal Chemical	Celogen	×	×	United States

[a]Addresses in the United States: Dong Jin (USA), Inc., P.O. Box 325, North Hampton, NH 03862; Miles Inc., Mobay Road, Pittsburgh, PA 15205; Schering Berlin Polymers, Inc., P.O. Box 1227, Dublin, OH 43017; Uniroyal Chemical, Elm St., Naugatuck, CT 06770.
[b]Witco Corporation, 520 Madison Avenue, New York, NY 10022, markets the Ficel range of blowing agents in the United States. Outside the Americas and Japan, Ficel products are marketed under the Genitron registered trade name.
[c]Not supplied in the United States.

TABLE 20.2 Properties of PVC Blowing Agents (4, 5)

Compound	Azodicarbonamide[a]	p,p'-Oxybis(benzenesulfonhydrazide)
CA name	Diazenedicarboxamide	Benzenesulfonic acid, 4,4'-oxybisdihydrazide
CA registry number	123-77-3	80-51-3
Structure	$NH_2CON=NCONH_2$	$H_2NNHSO_2C_6H_4OC_6H_4SO_2NHNH_2$
Physical form	Fine yellow powder	Fine white powder
Specific gravity (20/20°C)	1.65	1.43
Bulk density[b]	0.5–0.65 tons/m^3	0.55–0.66 tons/m^3
Decomposition range,[c] °F (°C)	392–410 (200–210)	302–320 (150–160)
Heat of decomposition (cal/g, 1 atm)[d]	150	—
Flammability hazard	Burns when exposed to flame; heating causes decomposition	Flammable solid easily ignited; heating causes decomposition
Storage stability	Stable below 50°C	Stable below 50°C

[a]Also called azobisformamide.
[b]After settling, depending on grade.
[c]In a capillary tube.
[d]Increases at higher pressure.

As might be expected by examining the foregoing reactions, the composition of the gaseous products will vary with decomposition temperature and environment, but can be broadly expected to be as follows:

Nitrogen	62 wt%
Carbon monoxide	35 wt%
Others (including ammonia)	3 wt%

The total gas yield represents 32–34% by weight of the azodicarbonamide. The composition of the gas can be shown to vary according to the conditions under which the azodicarbonamide is decomposed. The following data show how the composition of the residual solids can vary from the decomposition in two widely differing environments:

Solid Residue	AC Powder	AC Dispersion in Plasticizer
Urazole	39 wt%	27 wt%
Biurea	2 wt%	34 wt%
Cyanuric acid	25 wt%	5 wt%
Urea and ammonia salts	Some may be present	

The decomposition and consequent gas evolution from azodicarbonamide is a function of both time and temperature. If it is heated isothermally, both the rate and volume of gas generated increases with an increase in temperature as shown in Figure 20.2.

Although the gas yield in certain circumstances can be as much as 230 ml/g, in most expansion processes the yield does not exceed 200 ml/g.

The rate of gas evolution can also be shown to increase with a decrease in the average particle size. This effect may be due to the faster heat transfer through the smaller particles causing them to decompose earlier. Alternatively, it is proposed that interaction between the activator and the
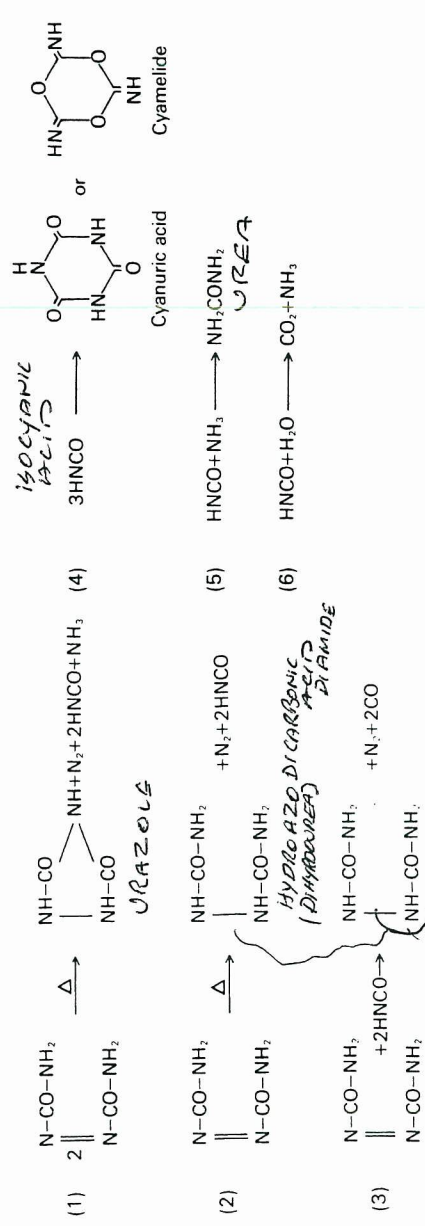
(1) $\quad$ 2 $\overset{\displaystyle N-CO-NH_2}{\underset{\displaystyle N-CO-NH_2}{\|}}$ $\xrightarrow{\Delta}$ $\overset{\displaystyle NH-CO}{\underset{\displaystyle NH-CO}{\Big\rangle}}NH+N_2+2HNCO+NH_3$ $\quad$ (4) $\quad$ 3HNCO $\longrightarrow$

URAZOLE $\qquad$ *IZOCYANIC ACID*

Cyanuric acid $\qquad$ or $\qquad$ Cyamelide

(2) $\quad$ $\overset{\displaystyle N-CO-NH_2}{\underset{\displaystyle N-CO-NH_2}{\|}}$ $\xrightarrow{\Delta}$ $\overset{\displaystyle NH-CO-NH_2}{\underset{\displaystyle NH-CO-NH_2}{|}} + N_2 + 2HNCO$

HYDRAZO DICARBONIC ACID DIAMIDE (BIHYDROUREA)

(5) $\quad$ HNCO+NH$_3$ $\longrightarrow$ NH$_2$CONH$_2$ $\quad$ *UREA*

(3) $\quad$ $\overset{\displaystyle N-CO-NH_2}{\underset{\displaystyle N-CO-NH_2}{\|}}$ + 2HNCO $\longrightarrow$ $\overset{\displaystyle NH-CO-NH_2}{\underset{\displaystyle NH-CO-NH_2}{|}} + N_2 + 2CO$

URAZOLE

(6) $\quad$ HNCO+H$_2$O $\longrightarrow$ CO$_2$+NH$_3$

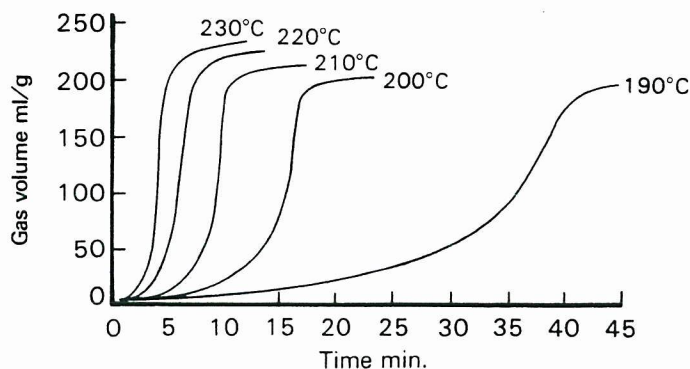**FIGURE 20.1** Decomposition reactions of azodicarbonamide.

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FIGURE 20.2   Gas evolution of azodicarbonamide heated isothermally.
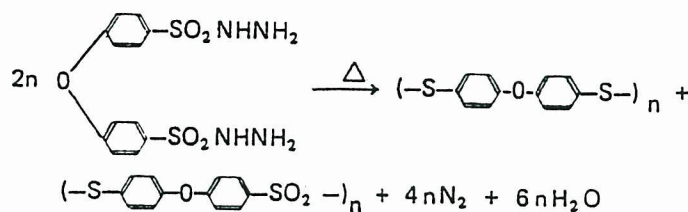

FIGURE 20.3   Assumed decomposition mechanism of OB.

AC is more efficient where the particle size is smaller, and the surface area of the AC is larger as a result.

p,p'-Oxybis(benzenesulfonhydrazide) (OB) decomposes at around 150°C, without first melting, liberating a gaseous mixture of nitrogen and steam. The noncondensable gas yield is 125 ml/g. The solid residue is a complex mixture of polymeric sulfur-containing products. The exact decomposition mechanism is uncertain, but by analogy to a related compound, benzenesulfonylhydrazide, it is assumed to be as shown in Figure 20.3. The condensable gases (i.e., water vapor) and the solid residue together represent approximately 84% of the original OB used.

20.5   AZODICARBONAMIDE GRADES

Variations in particle size of the blowing agent give rise to grades with differing expansion properties. In another modification, the surface properties of the powder can be altered to give grades with improved dispersibility. Also, the decomposition temperature of the azodicarbonamide can be reduced by activators. Furthermore, the decomposition reaction products can be altered by various compounds which react preferentially with the isocyanic acid before trimerization occurs. All these factors result in a large number of grades of azodicarbonamide.

20.5.1   Particle Size

When comparing the particle size of grades from different manufacturers, it is important to know the method of measurement. Some techniques differ widely both in their principles of measurement and in the results obtained from identical samples.

Establishing particle size using sieves is not possible even with the coarsest of AC grades,

because the particle size is too small. The Fisher Sub-Sieve Sizer is established in some industries. This technique measures the air permeability of a compacted plug of powder sample and then derives the figure for average particle diameter. In the case of AC powders, this results in a lower figure than would be obtained with most other methods. For fine grades of AC, a Fisher particle size is about half that obtained from most other methods. A wide range of instruments which use volume displacement of electrolyte or optical methods to measure particle size are now available (6). These instruments usually have data processing packages which also allow particle size distribution to be seen.

Coarse particle size grades are typically in excess of 12 microns average particle diameter as measured by electrolytic displacement (Coulter method). Intermediate particle size grades fall in the range of 8–12 microns, and fine particle size grades are less than 8 microns.

Some examples of commercially available grades are as follows:

COARSE PARTICLE SIZE

Celogen AZ 180	Ficel 18/27
Porofor ADC/E	Unicell D2500
Unifoam AZ-H	

INTERMEDIATE PARTICLE SIZE

Celogen AZ 150	Ficel AC2
Porofor ADC/F	Unicell D900

FINE PARTICLE SIZE

Celogen AZ 120	Celogen AZ 130
Ficel AC3	Ficel AC4
Porofor ADC/M	Unicell D300
Unifoam AZ-25	

The finer particle grades are more commonly used in the PVC industry. Powders in this class have a cohesive nature—that is, they do not flow readily through powder-handling equipment. Furthermore, these powders cannot be added directly into low-shear mixers because adequate dispersion is not achieved in this way, especially in low-viscosity plastisols. This necessitates making a premix of the AC with plasticizer on high-shear equipment such as a three-roll mill or dissolver-type mixer—an operation viewed with distaste by some processors for its messiness and additional cost. Dispersible grades of AC were developed to meet the need for improvement in this area.

20.5.2 Dispersibility

Improvement in dispersibility is achieved by one of two principal methods: coating of the particles with compounds more compatible with the PVC mix, or by addition of very-small-particle-size silicas. The result in each case is a more flowable powder which can be added directly to plastisols under normal mixing conditions. Typical grades include the following:

Celogen AZ 2990	Celogen AZ 3990
Ficel AC-SP4	Ficel AC-SP5
Unicell D300 SD	

The azodicarbonamide content of these products is invariably greater than 95%, and particle size is similar to unmodified AC grades; thus expansion performance is not significantly changed.

20.5.3 Other Modifications

AC grades are also available which usually have been modified for a particular application, and this determines the nature of the other ingredients.

Activated grades incorporate special activators at the time of manufacture. This ensures intimate contact between the two ingredients and gives certain property improvements such as more rapid decomposition or whiter foams. Of advantage to the materials manager is reduced inventory, since one ingredient is needed instead of two or three. To production, these materials bring increased line speeds, or the ability to process at lower temperatures. Highly activated grades allow chemical foam production at much lower temperatures than in conventional systems, thus offering new capabilities for development of vinyl products. The finished foam is whiter, which can be a benefit to the consumer; or if no change in color is desirable, the level of titanium dioxide can be cut back and cost savings achieved (7, 8). Examples of products in this category include the following:

Ficel SCE—a co-activated grade which processes at conventional temperatures [180–220°C (360–430°F)]
Ficel LE—a highly co-activated grade which processes at low expansion temperatures [150–200°C (300–390°F)]

Typical results with a highly co-activated grade of AC are shown in Figure 20.4, demonstrating a means to achieve higher line speeds at conventional processing temperatures.

Anti-plateout grades may be required when AC is used in extrusion and injection-molding processes. Fortunately, the decomposition residues are more soluble in PVC than in other polymers, so this is seldom a problem. Some typical grades include the following:

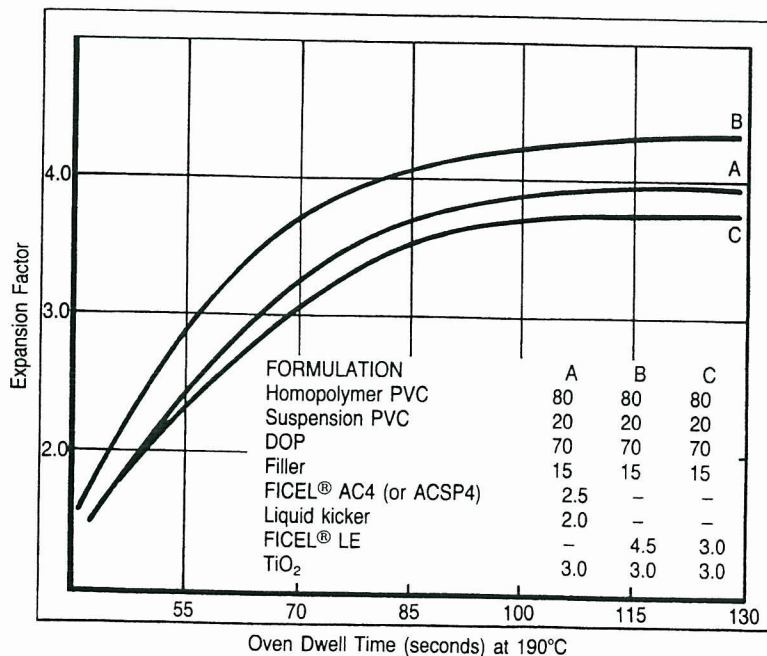Celogen AZNP
Ficel EP range
Unicell D300 NP

FIGURE 20.4 Comparison of highly co-activated and conventional AC blowing agents.

20.6 REDUCING DECOMPOSITION TEMPERATURE

As mentioned in Section 20.5.3, the temperature at which azodicarbonamide decomposes can be reduced by the addition of activators. The most effective activators include the following:

Transition metal compounds

Amines, amides, and glycols

There are many proprietary formulations containing transition metal compounds which, although being sold primarily as PVC stabilizers, will exert an activating effect on azodicarbonamide. Because of this these stabilizers are sometimes referred to as "kickers." The extent of the activating effect depends on the nature, concentration, and physical form of the metal compound present.

Zinc-, cadmium-, and lead-containing compounds are the most effective activators and are generally used in the form of oxides, salts (usually of a fatty acid), or other organometallic compounds. Liquids, such as the metal octoates, will have enhanced contact with the azodicarbonamide, and this will increase their activating properties.

Those metal compounds based on cadmium and lead are found to be more effective than zinc where decomposition in the 160–180°C (320–356°F) range is required, whereas zinc gives a more rapid decomposition above 180°C.

Other metal compounds which may be present in proprietary stabilizers, such as calcium, barium, potassium, or tin, could have activating effects, but these will be weak in comparison.

Gas yields obtained with compounds containing zinc or cadmium activators are about 190 ml per gram of azodicarbonamide. Lead activators may reduce this yield to around 160 ml.

Although decomposition temperature can be reduced to as low as 125°C (257°F), useful decomposition rates are usually only achieved at 160°C (320°F) and above.

When an activator for the AC is not desired, one can use either (a) a barium stabilizer with epoxidized soybean oil or (b) a tin stabilizer.

It is also possible to reduce the decomposition temperature of sulfonhydrazides. Addition of an equal quantity of a suitable grade of urea can reduce the decomposition temperature from 150°C (302°F) to 125°C (257°F). Metal compounds, such as zinc oxide and ferric chloride, are also activators for sulfonhydrazides.

20.7 DISPERSION IN POLYMER MIXES

For efficient use of a blowing agent, and to ensure that a uniform cellular structure is obtained in the foam, it is important to achieve good dispersion in the polymer. Azodicarbonamide is insoluble in plasticizers and in all common solvents, so there is no practical way in which it can be added to compounds in solution form.

Where polymer granulate is the starting point, it may be possible to coat the granules with a small amount of a suitable liquid (0.5%), such as a plasticizer, and then tumble the predamped granules together with blowing agent powder. The blowing agent is then dispersed within the barrel of the injection molder or extruder during processing. This method is limited to fairly low levels of blowing agent. It is preferable in these applications to use polymer-bound masterbatch, and this has the advantage of avoiding dust in the machine area. Liquid dispersions can also be used.

Addition of unmodified grades of AC into plastisols is accomplished by preparing a pre-paste of the AC in plasticizer using a high-shear mixer. A 50% dispersion of fine-particle AC in DOP produces a soft, nonflowable paste which can then be added to the bulk plastisol during mixing. Production of pre-pastes can also be accomplished using three-roll mills, or similar equipment. Quality of the pre-paste is readily checked using a fineness-of-grind gauge.

Dispersible grades of AC are added as powders directly into the plastisol mixer. Certain min-

imum conditions of shear and circulation of mix are necessary for optimum dispersion; usually these are easily met. However, a sensible precaution is to pass the mixed plastisol through a filter with a mesh of 200-micron aperture or less.

20.8 EFFECT OF INGREDIENTS AND PROCESSING ON PLASTISOL FOAM QUALITY

Plastisols are the most important type of compounds used in manufacturing foamed vinyl products. The following general discussion on plastisols applies to products expanded at normal atmospheric pressures in coating applications. High-pressure processes are dealt with more fully in subsequent sections.

Before examining the effect of different ingredients in a plastisol on foam quality, it is necessary to appreciate the difference between gelation and fusion (9). If a metal plate is heated to say 240°C (464°F) at one end and the other end is at room temperature, a temperature gradient will develop along the plate. If a plastisol is spread in a film along the plate, there will be a minimum temperature where the plastisol becomes dry but is totally lacking in strength. This is known as the *hot bench gelation temperature* (Chapter 34, ''Laboratory Compounding and Test Methods''). Continuing along the plate toward the heated end, the plastisol remains in the gelled state until a point is reached where useful physical properties begin to develop. The plastisol is considered fused at that point. However, to be fully fused (i.e., to achieve maximum physical properties), it is necessary that a certain minimum elevated temperature beyond that point be achieved. Prolonged heating at a lower temperature will not suffice (10).

Blowing Agents The blowing agent system should be designed to start generating gas between the fusion temperature and the oven temperature. In contrast to plastisol fusion, there is a distinct time–temperature–concentration relationship for the blowing agent system:

- Increasing oven residence time will increase gas evolution up to a maximum level as determined by the blowing agent concentration.
- Increasing blowing agent concentration will increase both rate and volume of gas generation. High concentrations of blowing agent can also have the effect of decreasing the temperature at which gas starts to be generated; this is also true of increased kicker concentrations. Higher kicker loadings will increase the rate of gas generation, but they will not increase the gas volume and may even cause a reduction.
- Increasing temperature will increase rate of gas generation and may also slightly increase gas volume (11).

There are several ways of representing these relationships; most commonly used in coating applications is a time–thickness graph. Increase in thickness can also be described as expansion factor (EF) or blow ratio, which is defined as foamed thickness divided by thickness applied. This number is useful in coating applications. However, density is the most universal measurement and is meaningful for irregularly shaped articles. The relationship between density and expansion factor is:

$$\text{foam density} = \text{unfoamed density}/\text{EF}$$

Figure 20.5 shows how blowing agent particle size and oven dwell time influence expansion factor. The faster rate of decomposition mentioned earlier for finer-particle-size blowing agents is apparent.

Loadings of blowing agent and kicker are typically in the range of 1–10 phr. Some examples are shown in Table 20.3.
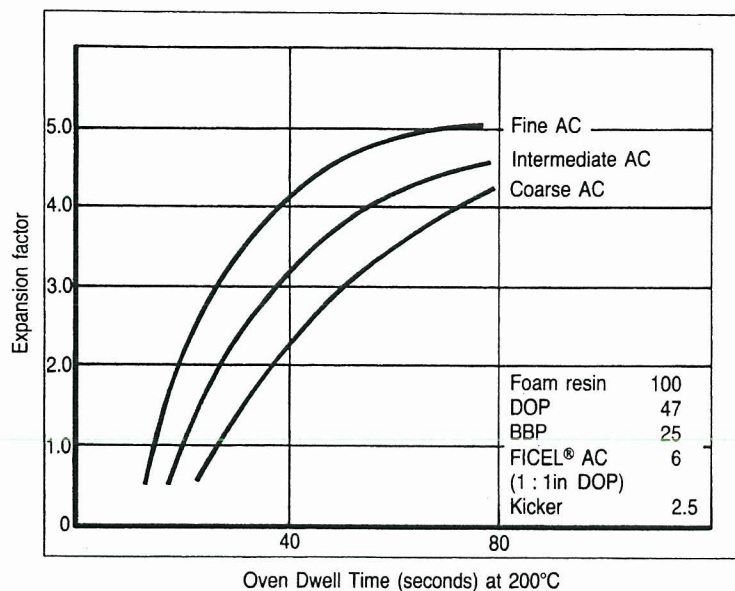
FIGURE 20.5 Effect of AC particle size and oven dwell time on expansion factor.

PVC Resin Key considerations in the selection of the PVC grade are the desired physical properties, foam quality, and any process limitations, including fusion characteristics and rheology. It is important that the blowing agent decomposes while the polymer is properly fused. If gas is evolved before fusion, it will be lost from the film instead of being contained by it. The result of this is seen in a lower-than-expected expansion thickness, a rough irregular surface, and poor cell structure.

If the intended process imposes time–temperature limitations, one approach to increase fusion rate would be to select a low-fusion resin. This might be one of the lower-molecular-weight homopolymers, or a copolymer resin. However, in solving the fusion problem, care must be taken so that other problems are not created—for example, those involving viscosity stability or an unacceptable decrease in tensile properties. This may require other adjustments in the formulation—for example, changing the plasticizer system, using a different filler or filler level, etc.

Other characteristics of plastisol-grade PVC resins also affecting fusion include particle size, emulsifier type, and alkalinity. This helps explain why similar-molecular-weight PVCs can give quite different foam qualities (12).

The use of extender grades of PVC is common, both to lower plastisol viscosity and to reduce cost. In many cases, especially when used at low levels (e.g., 10–20% replacement), this has no

TABLE 20.3 Some Typical Loadings of Blowing Agent and Kicker/Stabilizer

Expansion temperature		Blowing agent	Phr	Kicker/stabilizer	Phr	Possible end uses
°C	°F					
200–180	392–356	Ficel AC4	2	Potassium/zinc liquid	1	Coated fabric
200–180	392–356	Ficel AC4	3	Zinc oxide	1	Wall Coverings
200–180	392–356	Ficel SCE	4	None required[a]	—	Sheet flooring
170–150	338–302	Ficel LE	5	None required[a]	—	Sheet flooring backing

[a]Stabilizer/kicker is in blowing agent composition.

noticeable effect on foam quality. However, in difficult formulations, an improvement in cellular structure can sometimes be seen when extender resin is backed out of the formulation.

Plasticizer Aside from the PVC resin, plasticizers also have a marked effect on fusion temperature. Thus, a problem with late fusion can often be resolved by substituting a fast solvating plasticizer, such as dihexyl phthalate or butyl benzyl phthalate, for a portion of the primary plasticizer. However, attention must be paid to the rheology of the plastisol, including storage stability, when making such a substitution. Also, fast solvating plasticizers tend to be volatile, and this must be considered.

Conversely, where it is desired to use the less volatile and slower fusing plasticizers, such as DINP or DIDP, slightly higher processing temperatures may be needed and it may be necessary to slightly reduce the activation of the blowing agent (10).

Depending on the activity of the blowing agent system, there is a lower limit to plasticizer concentration for a given level of blowing agent. In this case, either the plasticizer level can be increased (if this can be tolerated in other respects) or the blowing agent activity can be decreased. For example, at plasticizer levels of 45 phr, fast expansion systems may give satisfactory foam quality up to expansion factors of 3, whereas at 55 phr plasticizer, expansion factors of 4.5 could be achieved. This relationship is also dependent on blowing agent activity and temperature. In hard foams with low plasticizer levels, it is possible that the blowing agent may decompose before full fusion is reached, resulting in poor foam quality.

Heat Stabilizer As discussed in Section 20.6, most heat stabilizers have a significant effect on the decomposition temperature of chemical blowing agents, and this needs to be remembered when formulating with AC as well as with OB. Furthermore, co-activated grades of blowing agent usually confer sufficient processing heat stability themselves and should not be used with additional activating heat stabilizers.

Fillers Calcium carbonates do not interfere with chemical blowing agents and are widely used. Work has been carried out which indicates that loadings around 30 phr can result in optimum indentation recovery of the foam (13). However, care should be taken to avoid deterioration of foam quality at high loadings of calcium carbonate. Typical loadings range between 10 and 40 phr in foamable plastisols.

Other Ingredients Low levels of 2,2-bis(4-hydroxyphenyl)propane (BPA), the antioxidant contained in some electrical-grade plasticizers, can cause strong coloration when used with azodicarbonamide blowing agents. The foams have a pink or brown color from reaction of the AC decomposition intermediates with the BPA, and the color intensity increases progressively as the AC decomposes. The actual color of the foam also depends on the type of metal ions present, suggesting that formation of a metal complex is also involved (reference 10, Chapter 18, "Antioxidants").

When the antioxidant in the plasticizer causes color formation, the simplest approach is to obtain an uninhibited grade because the antioxidant is unnecessary in most applications. Alternatively, certain highly effective hindered phenol antioxidants are available which do not react with azo compounds—for example, Topanol CA (Chapter 18, "Antioxidants").

Certain grades of heat stabilizers can also cause coloration problems due to the presence of an unhindered antioxidant in the stabilizer package.

If problems of this sort are encountered, a simple screening test to identify the ingredient involved is to mix the AC and kicker with the suspect ingredient in a test tube. The test tube is heated to decompose the AC, and the contents are visually examined for color formation (14).

Addition of viscosity depressants is sometimes needed. Certain proprietary products based on surfactant blends can interfere with activation of the blowing agent and thus should be used at minimum levels.

Processing Conditions A number of processing conditions will affect expansion and foam quality. The importance of producing a mix with good dispersion has already been discussed. In addition, deaeration of the plastisol before spreading can possibly further improve foam quality.

A useful feature of chemical blowing agents is that they allow gelation of the coatings before foaming occurs. This allows printing of the surface and multiple coating operations. Gelation temperatures should be kept well below expansion temperatures to avoid premature decomposition. However, this rule is broken where mixed blowing agents are used to achieve texture. Gelation temperature is chosen so that the lower-temperature blowing agent starts to decompose early, causing small voids in the coating which are subsequently expanded during the main expansion.

Expansion temperature clearly has a dominating effect on time required for foaming. The importance of the oven is not well appreciated. Because of more efficient heat transfer, high-air-velocity ovens are the best type for chemical foaming processes. Degree of expansion can also be controlled by residence time in the oven. When all the blowing agent has decomposed, no further increase in thickness will occur. It is undesirable to have oven dwell times longer than this; otherwise, cell structure deteriorates and foam thickness can decrease. Furthermore, output rates will decrease, and embossing depth will suffer in the chemical inhibition process.

20.9 FOAMED COATED FABRICS (LEATHERCLOTH) (15)

The advantages of these products over unfoamed coated fabrics include better suppleness, draping, and stretching properties as well as improved handle (hand). The products are very similar to real leather and are considerably lower in price (16).

The construction generally comprises a fabric support, with a foam layer between this and a solid top wearcoat. Choice of fabric determines the strength, while variation of the wearcoat and expanded layers alters the handle and wear properties of the material. Foam density and thickness, as well as plasticizer loading, are further factors which all result in a wide range of final products.

Spread coating can be carried out directly onto dimensionally stable tight-weave fabrics. However, this method has the difficulty that when the foam is expanded, the fabric texture "telegraphs" through to the top surface, necessitating an extra coating and embossing operation to achieve a smooth surface on which to coat the expandable layer. Transfer coating is more versatile. In this method the plastisol layers are spread onto specially textured release papers or onto a continuous belt, and the fabric is then laminated on. This technique allows use of a wide range of fabrics and surface finishes; however, the release paper wears out and must be replaced regularly, which adds cost to the finished product.

Some grades of leathercloth, such as those used for luggage, need to be hardwearing. This requires a stiff, low-plasticizer-content foam. The activator and its addition level must be especially carefully chosen to match the total formulation and processing conditions to be used. Melt viscosity at expansion temperature is important. It can be increased (for example) by the use of a higher-K-value PVC, by lowering the plasticizer content, or by lowering the expansion temperature. In these cases, a slower activator will be required to retain good foam quality and to prevent blistering. Alternatively, a coarse grade of AC could be used.

With copolymers, it is possible to produce foams at 150–160°C (302–320°F) using highly activated blowing agents. This permits the use of temperature-sensitive substrates, such as polypropylene fiber fabrics, which do not otherwise lend themselves to foaming processes.

Typical starting place foam coat formulations are shown in Table 20.4, including one designed for low-temperature fusion.

Unsupported products—for example, those without fabric backing—are used in certain automotive applications. The material is heated and thermoformed onto fiberboard panels. This is a severe test of foam quality, and dimpling is seen with poor-quality materials. Where this occurs, increasing foam density is an effective remedy. Use of cross-linkable PVCs has also been proposed, but these are not widely available (17).

TABLE 20.4 Typical Starting Place Foam Coat Formulations

Grade	Upholstery	Luggage	Low fusion temperature
PVC homopolymer (dispersion grade)	100	100	—
PVC copolymer (dispersion grade)	—	—	100
DOP	80	—	45
DINP	—	65	—
BBP	—	—	30
CaCO$_3$ filler	5	20	15
AC (coarse grade)	—	3	—
AC (fine grade)	3	—	—
Ficel LE	—	—	4
Liquid kicker/stabilizer (fast)	2	—	—
Liquid kicker/stabilizer (slow)	—	2	—
Colorant	As required	As required	As required

20.10 FLOOR COVERINGS

Plastisol-based processes have made possible the production of a wide variety of flooring products. These products are multilayered constructions, the simplest having four layers. Several techniques for their manufacture can be utilized as described in the following.

Mechanical Embossing In the first stage of this technique, a layer of foamable PVC plastisol is spread onto the appropriate substrate and passed through an oven to gel the plastisol without decomposing the blowing agent. The resulting coating is subsequently printed with the required design, usually by rotogravure methods using solvent or water/alcohol inks. This is followed by application of a clear plastisol top coat, and the material is immediately passed through an oven at elevated temperatures. At this stage the blowing agent decomposes and the resulting gas is trapped in the PVC matrix, producing the foam. Immediately at the exit of the oven the surface is smooth; texture is obtained by promptly embossing the material using a heavy sculptured roller which compresses the foam in those areas where the contour of the embossing roller stands proud. The design of the embossing roller can vary according to the pattern. It is possible to manufacture products where the embosser is designed to match the printed design. On the other hand, simpler random embossing can be used to produce a more restricted design range which is devoid of the difficult problem of exactly synchronizing the embossing to the preprinted design. Fine-particle-size grades of AC tend to be used in this process.

Chemical Embossing In this technique the initial substrate coating is as described previously; that is, the pre-gelled vinyl sheet is produced ready for the printing stage. In some of the printing inks, however, an inhibitor is added which retards decomposition of the blowing agents. Suitable inhibitors are benzotriazole and tolytriazole, which offer good results in both solvent and water/alcohol inks; others include trimellitic anhydride and fumaric acid (18).

After the printing stage, the vinyl topcoat is applied and the web is fed through the high-temperature oven, causing the foam to form. Unlike that made by the mechanically embossed route, the product emerges from the expansion stage complete with the preprinted sculptured design. The inhibitor blocks the effect of activators on the blowing agent decomposition, and there is no requirement for the additional stage of mechanical embossing.

When unactivated grades of AC are selected, the kicker of choice is zinc oxide at 30–50% of the AC level by virtue of its good response to inhibition. However, use of this kicker has several drawbacks. First, it is not very active and line speeds can be restricted. Second, due to the inefficient kicking action of zinc oxide, the final foam coloration is not very white. This phenomenon may be associated with residual, unreacted AC persisting in the foam even after the expansion

stage. Evidence suggesting this to be the case is shown by the fact that exposing the foams to ultraviolet light leads to a marked increase in whiteness. Third, while dispersible grades of AC and titanium dioxide are available and allow streamlining of production (by avoiding production of pre-pastes), similar grades of zinc oxide are not presently available. Consequently, pre-pasting cannot be eliminated altogether.

Patented developments in blowing agent technology have resulted in more efficient activated azodicarbonamide systems becoming available. In such systems, kicker choice and manufacturing route are extremely important. Successful harnessing of this technology results in systems which offer better performance by promoting a much more efficient decomposition of the AC; this may be a different mechanism than with an externally added kicker. An example of a product of this type is Ficel SCE. Use of this type product has a number of advantages:

- Greater expansion efficiency while retaining excellent inhibition
- Improved color, or achieving cost savings
- Easier dispersibility

A comparison of a conventional AC–ZnO system with this more efficient system is shown in Figure 20.6.

Screen Printing In this technique a totally different method of printing dictates the exact construction of the product. Instead of the rotogravure method described previously, a foamable plastisol ink is applied through a hollow cylindrical mesh screen. By a variety of methods it is possible to block specific areas of the screen, thereby producing the required design. The thickness of the film or ink deposit in the screen printing technique is significantly greater than in rotogravure (typically 6 mils compared to 0.4 mils). As with the gravure machines, up to eight printing stations can be used. However, in the screen technique separate oven zones are required between printing heads to pre-gel the plastisol before the next printing head.

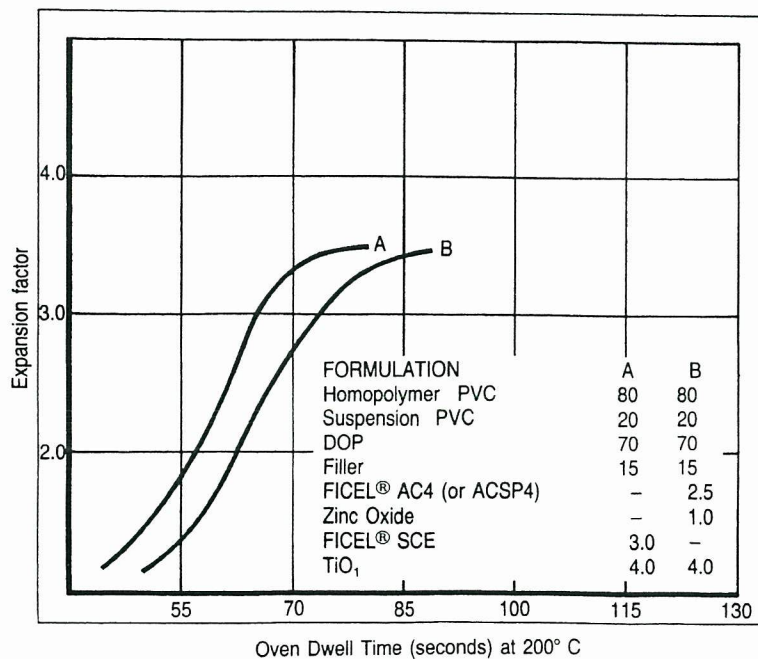| FORMULATION	A	B
Homopolymer PVC	80	80
Suspension PVC	20	20
DOP	70	70
Filler	15	15
FICEL® AC4 (or ACSP4)	–	2.5
Zinc Oxide	–	1.0
FICEL® SCE	3.0	–
TiO_1	4.0	4.0

Oven Dwell Time (seconds) at 200° C

FIGURE 20.6 Comparison of conventional AC–ZnO system with more efficient system.

The all-important surface texture can be obtained in two ways when a screen printing machine is used:

In one technique, a suitable blowing agent can be incorporated into the pigmented plastisol ink. This ink is then printed directly onto a precoated substrate. After printing the desired number of colors to build up the design, a clear plastisol topcoat is applied and the product is then heated in an oven to fully fuse the topcoat and expand the preprinted foamable "inks."

The alternative combines screen printing and chemical embossing techniques. The screen-applied plastisol contains a low level (~3%) of inhibitor. This is printed onto a pre-gelled PVC sheet containing a suitable blowing agent. Exactly as described in the chemical embossing technique, the final expansion of the vinyl is retarded by the inhibitor and the desired sculptured design is produced. A lower level of inhibitor is possible in the ink with screen printing, since the weight of deposited ink is much greater than with the corresponding rotogravure technique.

The variety of manufacturing techniques described in this section has developed to suit the needs of the market. In addition to the normal equation of capital cost versus efficiency and output, a careful study of the current patent situation in the country of manufacture, as well as in the countries where the product will be sold, must also be considered.

The two rotogravure techniques—mechanical embossing and chemical embossing—require significantly higher capital expenditures than do the screen printing techniques. The mechanical embossing technique requires an extra process step and is generally regarded as more expensive in final product cost terms than the more elegant chemical embossing method. The cost of rotary screens is less than that of printing cylinders; however, screens are not usually made for widths greater than 6 ft (2 m). The trend toward the wider 12-ft (4-m) floor coverings will ensure the dominance of rotogravure techniques for the foreseeable future.

Backings for Floor Coverings The continued success of glass-fiber-based products has demanded a new family of vinyl backings which are used to add thickness and resilience to the product. The nature of the construction of the final product has required the backing to be applied after the expansion of the embossed decorative foam. Because of this, narrow temperature limits must be observed for applying the backings in order to ensure that the product, which is inverted to apply the backing, does not suffer face damage in the fusion oven. The mechanically embossed route of production does not lend itself to application of most backings, because the temperature required to fuse the backing allows the embossed vinyl to soften and "recover" from the mechanical action of the embosser.

Three types of backings have emerged—solid, mechanically frothed, and chemically foamed:

1. The use of *solid backings*, being the simplest option, was the first route adopted in the initial stages of the introduction of glass fiber technology. Highly filled plastisols were spread-coated onto the back of the product and fused in the oven. This practice is still evident with thinner products in the low-cost sector of the market.

2. *Mechanically frothed foam backings* are made by first whipping air into the plastisol which is then coated on to the product. Thickness can be built up in this way, both effectively and at a reasonable cost. The froth density is limited by the design of the mixing machine and by its strength such that it will not collapse at the coating knife or in the oven. Typical densities are 0.6–0.8 g/ml. Nevertheless, the technique yields good-quality foam, albeit high in froth density, and the finished product has a smooth back. However, apart from vinyl fusion, additional energy is required to raise the temperature of the insulating air in the froth. In thicker coatings this effect becomes more noticeable. In addition, adhesion of the backing foam layer to the top layers is often not as good as with chemically produced foams, and water uptake can be significant because of the substantially open-celled structure.

A cost analysis of chemical versus mechanical foams is likely to be in favor of the chemical foam for the reasons discussed in the foregoing. These factors will outweigh any differences in the plastisol coatings because the level of foaming agent in each case is relatively low.
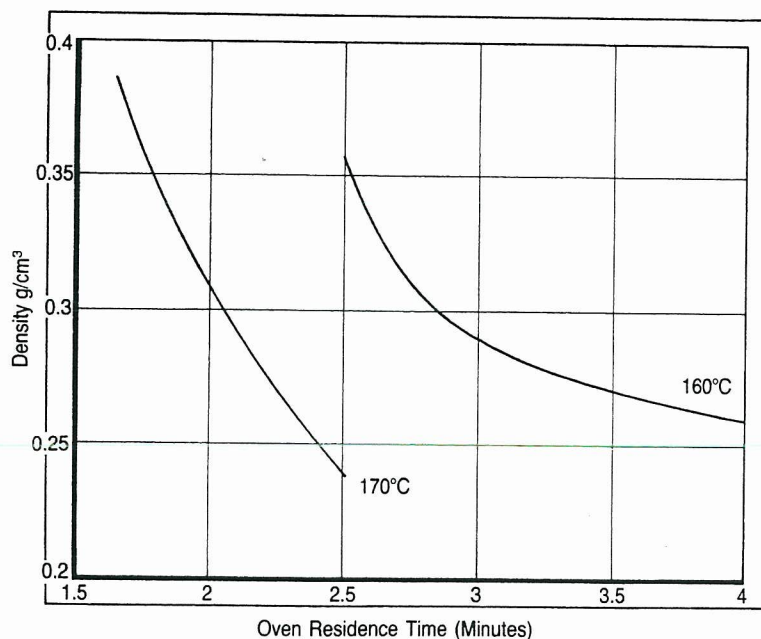
FIGURE 20.7 Foam density of low foaming temperature chemical foam at 160 and 170°C. Formulation: PVC–acetate (5% acetate)—100, DOP—40, BBP—30, filler—15, Ficel LE—5, TiO_2—2.

3. Until recently, *chemically foamed backings* had been unknown because of the problems of specifying a suitable chemical blowing agent which gives sufficient gas at the low temperatures demanded by the process. However, the development of blowing agent compositions based on azodicarbonamide with integral kicker has overcome this problem, and finished products are now produced using this blowing agent. A vinyl plastisol containing 4–5 phr of this type product will foam easily at 180°C (356°F). By using a 5% vinyl acetate copolymer resin, good results may be obtained at temperatures as low as 160°C (320°F) with obvious energy saving benefits. The densities obtained are in the 0.3- to 0.6-g/ml range, and the foaming thickness acts as a simultaneous check on the efficiency of the fusion—an obvious benefit over mechanical frothing.

Performance of a low-temperature chemical foam plastisol is shown in Figure 20.7.

20.11 WALL COVERINGS

Vinyls have been well established in the wall coverings industry for many years because of their superior physical strength, washability, and general durability compared to paper. The addition of blowing agents to the vinyl matrix led to the development of textured and sculptured effects. The reduction in density offered by the use of blowing agents also resulted in a very cost-effective method of adding thickness. The increasing popularity of rotary-screen-printed expanded vinyls has been an additional factor in enabling these products to gain strongly in market share, especially in Europe and in exports from Europe to the United States.

At the same time that chemical embossing was being adopted by the flooring industry, similar products were being developed for wall coverings. Performance requirements are different in the two markets; wall coverings do not require the foot traffic and indentation resistance that is necessary in floorings, and constructions are much lighter. However, the principles of the chemical embossing process are the same as those covered in the preceding section.

One variation of the chemical embossing process which has found favor in wall coverings is the chemical activation process. In this process, azodicarbonamide without activator is incorporated in the coating plastisol in the normal way, but the activator is incorporated in the gravure printing ink. On passing through the expansion oven, only those areas under the activator expand and the final result is an apparently embossed product. To obtain identical results in the same pattern, using the activation and inhibition processes, it is necessary to use different printing cylinders, one being the negative image of the other.

Mechanical embossing of wall coverings is usually in a general or random pattern which does not aim to be in register with the design. Again, principles are similar to floor coverings as covered earlier.

Highly expanded and textured designs can be produced more readily using the rotary screen technique than with the gravure techniques.

Enhanced surface effects in wall coverings may be achieved by various methods, two of which are summarized as follows:

- The required effect may be obtained by using two blowing agents of different decomposition rates and temperatures. Thus, a mixture of fine AC and AC with integral kicker may be successfully used. This system has the added benefit of responding to inhibition by benzotriazole. Textured effects can also be obtained by mixing AC and OB, although this can prove expensive and does not respond to inhibition.
- Incorporation of small amounts of low-boiling liquids result in their evaporation during the expansion stage. This leads to a textured finish.

Specific processes, temperatures, polymer systems, and application weights have a major bearing on the exact structure of the finish obtained, but cellular structure is not so important because indentation recovery requirement is not so demanding. Hence, higher line speeds, higher temperatures, or more active blowing agents are encountered.

20.12 LOW-DENSITY FOAMS

Soft vinyl foams can be produced at densities down to 0.10 g/ml by plastisol techniques. Thicknesses produced vary from 40 mils to 1 inch (1 to 25 mm), the thicker foams being cut to produce thinner sections for use as cushioning materials. Thinner foams are produced in constructions with pressure-sensitive adhesive and release paper layers for use as draft seals around window and door frames. Harder foams coated on both sides with adhesive are used as adhesive pads or bonding materials.

A starting place formulation for a low-density foam is shown in Table 20.5.

TABLE 20.5 Starting Place Formulation—Low-Density Foam[a]

PVC (K 68–70) (dispersion grade)	100
DOP	102
Epoxidized soybean oil	5
Liquid zinc stabilizer	8
Azodicarbonamide (fine particle size)	8

[a]Expansion at 190°C (374°F) produces foams with density of 0.13 g/ml.

TABLE 20.6 Starting Place Formulation for Metal Closure Seals[a]

PVC (K 68–70) (dispersion grade)	100
DOP	55
Calcium carbonate	20
Azodicarbonamide–fine particle size	1
Zinc oxide (suitable grade for food contact)	0.3

[a]Expansion at 200°C (392°F) gives foams with density of 0.6 g/ml.

20.13 METAL CLOSURE SEALS FOR FOOD CONTACT

Both crown and screw closures use expanded plastisols to provide resilient seals on glass bottles and jars. Application of liquid plastisols allows the high production speeds which are necessary in this industry. Expansion factors are low, being just sufficient for the foam to fill small irregularities on the sealing surface. Foamed seals are especially useful for multi-trip containers, which can become damaged on the sealing surface with repeated use.

Azodicarbonamide is sanctioned for certain food contact applications and is the main blowing agent used whether or not food contact is involved. Uses of AC applicable to PVC are listed in the U.S. Code of Federal Regulations:

- 21CFR 177.1210, Closure sealing gaskets in contact with food
- 21CFR 175.300, Resins and polymeric coatings

Maximum permitted dosage is 2% in each of the foregoing applications.

The blowing agent activator also requires sanction for food contact use, which limits the choice to certain zinc compounds such as zinc stearate and zinc oxide. Fine-particle-size grades of AC are usually preferred for their greater expansion speed.

A starting place formulation for metal closure seals is shown in Table 20.6.

20.14 METAL COATING

Automotive applications other than leathercloth account for use of small quantities of blowing agents. Expandable plastisols are used in sealing and adhesive compounds to fill voids and ensure a good contact of plastisol with the metal surface. Underbody sealants are usually highly filled and therefore have high density. Interest in reducing this density in many areas, thereby achieving weight reduction, has resulted in some acceptance of foamed coatings.

Large volumes of unexpanded plastisol are used in coil coatings for conversion to steel cladding for building purposes. Interest has been seen in producing expanded coatings which can be mechanically embossed to produce surface texture. A problem which needs to be solved is compression of the foamed coating in the coil or during conversion into cladding. One possible solution would be expansion of the coating after conversion.

A starting place formulation for a typical metal sealing compound is shown in Table 20.7.

20.15 PRESSURE-EXPANDED FOAMS

This process can be operated with different formulations to produce semirigid or soft foams of high or low densities and almost totally closed cell structure. However, manufacturing costs are high because the process involves press molding and a second expansion step.

TABLE 20.7   Starting Place Formulations for Metal Sealing Compound

	A	B
PVC (K 70) (dispersion grade)	75	—
PVC copolymer (5% acetate) (dispersion grade)	—	75
PVC extender resin	25	25
DOP	70	50
DINP	70	50
CaCO$_3$ (coated)	70	—
CaCO$_3$ (uncoated)	50	20
Stabilizer (K–Zn)	2	—
Stabilizer (Sn)	—	2
Epoxidized soybean oil	3	—
Polyamino adhesion promoter	4	4
Thickener (silica-type)	2	—
CaO moisture scavenger (50% in DOP)	20	—
Blowing agent (Ficel SCE)	2	—
Blowing agent, low temperature (Ficel LE or OB)	—	4
Expansion temperature, °F (°C)	338 (170)	302 (150)
Expansion time, minutes	20	20
Expansion factor obtained	1.5	1.5

The principle of the method is first to make a plastisol [or for semirigid foams, a rigidsol (rigisol)]. Suitable molds are then filled with the paste, and the molds are placed in a high-pressure press to heat the paste to a temperature sufficient to decompose the blowing agent. At high loadings, the exotherm from the blowing agent decomposition can contribute significantly to the heat input. Thus when formulating with AC, it is advisable not to exceed loadings of 14 phr, and it is also advisable to activate the AC so that decomposition occurs well below the PVC degradation temperature (19). (A fine-particle-size AC activated with a zinc compound, such as zinc oxide or zinc octoate, is typically used.) After full decomposition is achieved, the mold is cooled and the solid preform is removed.

The second stage in the process is now to heat the preform to approximately 212°F (100°C). In so doing, the PVC softens and allows the entrapped gas to expand. Where a precise shape is desired, this process is best carried out in molds.

Products manufactured by this process include rigid building panels for insulation, buoyancy materials (such as fishing floats), soft and semirigid packaging, shock absorbing boat fenders, and anti-vibration materials.

20.16   EXTRUSIONS

A remarkably diverse range of end applications exists. It is possible to process PVC on both conventional and specialized equipment using either physical or chemical expansion systems. However, physical expansion systems are mainly used for polyolefins and polystyrenes, whereas chemical expansion systems dominate for rigid and flexible PVC cellular extrusions.

Two extrusion techniques are used commercially for the production of cellular profiles, pipes, and hollow profiles. These are commonly referred to as (a) "free expansion," where free expansion of the extrudate takes place beyond the die face, and (b) "controlled expansion," which involves mechanical constraint of the rate of expansion of the extrudate.

The main disadvantage of the free expansion technique is the problem associated with the inability to maintain melt pressure above the gas solution pressure—particularly in dies with a cross-sectional area exceeding 5 cm^2 (0.78 in.^{2}), or in complex sections.

The controlled expansion technique is the basis of the Celuka process (20). The main advantage of this technique is the ease with which extrudates having large cross sections can be made; also, surfaces of such extrudates generally tend to be hard. Another advantage is that it is possible to manufacture products with lower densities, a typical density for rigid PVC foam being 0.35 g/ml (22 lb/ft^3). This technique works on the principle of inward foaming. A hollow profile is produced by placing a mandrel within the die. On exit, the melt is prevented from expanding outwards by a calibration unit which is a cooled hollow section of internal shape machined to the desired dimensions. Foaming then takes place inwards and fills the hollow section.

While activated azodicarbonamide grades are generally used in the free expansion system, inorganics (such as sodium bicarbonate) are used for the controlled expansion system. The use of mixtures of inorganic and organic blowing agents presents new possibilities to overcome problems of moisture pickup generally associated with sodium bicarbonate.

The main application of foamed rigid PVC profiles is in the wood replacement sector where complex sections can be manufactured. Areas where improvements can still be made include the low degree of rigidity and the tendency for the foam surface to indent easily if the density of the product is below 0.8 g/ml.

Formulating Rigid Profiles Factors considered beneficial in formulating foamable rigid compounds include the following:

- Low-K-value resin
- Lubricating systems which permit early gelation, maximizing mechanical work on the compound
- Processing aids to increase the rate of gelation and also to increase melt elasticity
- Level of filler which enables a rapid setup after the die
- Selection of the correct stabilizer/activator in conjunction with systems based on azodicarbonamide
- Control of compounding temperatures during the production of dry powder blends and melt compounds to avoid pre-decomposition of the blowing agent

Based on the foregoing, a typical starting place formulation for a rigid PVC foam is shown in Table 20.8.

As in other areas, selection of the correct grade of blowing agent and heat stabilizer, or of the correct activated grade of AC, is critical. Typical examples are shown in Table 20.9.

Machinery Considerations Cellular profiles can be produced by the free expansion technique on standard single-screw extruders with L/D ratios of 20/1 to 25/1 and compression ratios of 2/1 to 2.5/1. Fast gelling formulations can pose a problem with L/D ratios above 25/1; low L/D

TABLE 20.8 Typical Starting Place Formulation for Rigid PVC Foam

PVC (K 58) (suspension grade)	100
Heat stabilizer	1.5
Lubricant	1.5
Calcium stearate	0.7
Processing aid	5
CaCO$_3$	5
Titanium dioxide	2
Blowing agent	0.3–0.5

TABLE 20.9 Typical Stabilizer and AC Combinations for Extruded Rigid Foams

Stabilizer type	AC blowing agent
Lead	Ficel AC4, Celogen AZ130
Calcium–zinc	Ficel EPC, Celogen AZRV
Barium–cadmium	Ficel EPA, Ficel EPD, Celogen AZNP
Tin	Ficel EPE
—	Ficel EPE + sodium bicarbonate (for non-lead-stabilized Celuka formulations)

ratios, on the other hand, give problems in attaining optimum melt conditions without pre-decomposition of the blowing agent.

Maintaining melt pressure above gas solution pressure is slightly less critical for rigid PVC compounds, and short convergent die lands assist in setting up the skin of the cellular extrudate. Die designs are such that melt pressure decay rates across the cross section are kept constant. Such conditions are attained by the use of several mandrels which do not extend beyond the die face for the production of complex section extrudates. The mandrels are positioned to ensure uniformity of wall thickness in the extrudate as it expands into the calibration unit, resulting in a reduction in post-expansion problems during the shaping operation. Calibration dies are normally operated in tandem due to the low levels of heat extraction from the cellular extrudate and to prevent compression during take-off.

Finishing operations can include wet printing, or foiling, depending on the end-use area.

Main Areas of Application   Cellular extrusion offers a production technique for manufacturing a range of extrudates in the form of sheets, profiles, and tubes. A range of densities with varying degrees of flexibility are possible. Areas of applications are continually increasing, and the introduction of co-extrusion increases this potential even further.

The main applications at present are shown in Table 20.10.

20.17 CALENDERING

Instead of producing expandable coatings by plastisol spreading processes, it is possible to produce thin expandable calendered film. The film is then laminated to a substrate such as wallpaper base. The substrate provides sufficient support for subsequent printing and expansion processes. In production lines, the blend containing AC powder is compounded in an extruder or an internal mixer before being fed into the calender. Temperature and shear conditions are high during compound-

TABLE 20.10 Main Applications of Cellular Vinyl Extrusions

Rigid applications

Profiles and co-extruded profiles in the building construction industry (e.g., foamed core pipe)

Low-pressure pipe systems (where legislation permits), including co-extruded pipe

Electrical conduit

Flexible applications

Sealing strips

Low-density pipe insulation (PVC–NBR blend)

ing, and care must be taken to avoid any decomposition of the blowing agent at this stage. Use of coarser-particle-size AC or slower activators will help avoid this problem.

20.18 INJECTION MOLDING

Injection molding of rigid PVC or its alloys has not yet been used successfully for foam applications, the main drawback being degradation of the resin resulting from heat buildup caused by high injection speeds. Development work is being carried out in this area, and possibilities exist in electronic applications.

Injection molding of plasticized PVC is, however, very common, and the major area of application is shoe soles. Special proprietary formulations have been developed for production of sports shoe soles, but formulations for production of "standard" shoe sole compounds tend to be fairly simple. However, selection of the proper blowing agent is critical to obtaining good foam quality. An activated grade is normally used to ensure full decomposition with machines typically operating at 338–347°F (170–175°C). The use of dry blends is possible, but they are not commonly used because problems from insufficient mixing of the melt are more likely to occur than with granulate. A typical starting place formulation is shown in Table 20.11.

20.19 *p,p'*-OXYBIS(BENZENESULFONHYDRAZIDE) (OB)

As noted earlier, this is the only other blowing agent that finds significant use in PVC in the United States. OB is supplied under the following trade names:

Celogen OT	Uniroyal Chemical, Division of Uniroyal, Inc.
Unicell OH	Dong Jin Chemical Industries Co.

OB decomposes at around 150°C (302°F), liberating a gas mixture of nitrogen and steam; this leaves a solid residue that is a complex mixture of polymeric sulfur-containing products.

Usually AC or a modified AC will be a more cost-effective choice than OB, so usage is limited to some small-volume specialized applications. For example, OB is a white powder; this can be an advantage in the formulation of white and light-colored products. Also, its relatively low decomposition temperature makes it a useful low-temperature blowing agent.

20.20 TROUBLESHOOTING GUIDE

Problems in foam production may arise in initial product development as well as in routine production. It is often possible to pinpoint, or at least narrow down, the probable cause of the problem by closely examining the foam with the naked eye or under a magnifying glass. Table 20.12 lists common problems encountered and some of the most likely causes.

TABLE 20.11 Starting Place Formulation for "Standard" Shoe Sole Compound

PVC (*K* 70) (suspension grade)	100
DOP	70
Epoxidized soybean oil	3
Ca–Zn soap-type stabilizer	3
Stearic acid	0.4
Activated grade AC (e.g., Ficel EPE)	0.4

TABLE 20.12 Common Foam Problems, Some Possible Causes, and Solutions

Problem	Possible causes	Solutions
Density too high	Insufficient blowing agent (BA).	(a) Increase BA loading slightly.
		(b) If BA liquid dispersion was used, check that no settling has occurred.
	BA loading is too high, and premature decomposition has occurred. In this case, a poor cell structure and surface will be seen.	(a) Decrease loading.
Irregular cell structure	PVC not fully fused when BA decomposes.	(a) Use lower K-value PVC or try a grade known to produce good foams, e.g. PVC–acetate copolymer.
		(b) Increase expansion temperature.
		(c) Use fast-fusing plasticizer (e.g., BBP).
		(d) Deaerate plastisol.
		(e) Reduce kicker level.
		(f) Use coarser-grade AC.
	Poor dispersion of BA.	(a) Use a dispersible grade of BA.
		(b) Check equipment and work methods of dispersion process.
Discolored foam	Interaction with antioxidant (Section 20.8).	(a) Use plasticizer without antioxidant.
		(b) Use stabilizer without antioxidant.
	Use of a zinc-sensitive grade of PVC.	(a) Change PVC grade.
		(b) Change to a zinc-free activator.

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