BLOWING AGENTS

Reprinted from

Encyclopedia of Polymer Science and Technology

BLOWING AGENTS

The term blowing agents applies to substances that can produce pores or cells in polymeric compositions. If the cells are formed through a change in the physical state of the substance—ie, through an expansion of a compressed gas, an evaporation of a liquid, or by the dissolving of a solid—the material is called a *physical blowing agent*. If the cells are formed by liberation of gases as products of the thermal decomposition of the material, the material is called a *chemical blowing agent*. The methods of using the blowing agents described in this article are discussed under CELLULAR MATERIALS.

Historical Background

The use of blowing agents to produce cellular bodies based on high polymers goes back to the early days of rubber technology. In 1846, just a few years after the discovery of vulcanization, Hancock and others received several patents (1) covering the process of making natural rubber sponge using ammonium carbonate and volatile liquids as blowing agents. Not until 1856, however, was rubber sponge produced on a limited scale in England (2) and offered commercially for a variety of end uses. In the United States, large-scale production of rubber sponge for household use began around 1902. A. C. Squires of B.F. Goodrich Co. (3) developed a rubber compound containing ammonium carbonate that yielded sponge with large, interconnected cells. In the 1920s the introduction of efficient rubber accelerators and antioxidants significantly contributed to the rapid growth of sponge-rubber goods for industrial and household applications. At that time the carbonates in various physical forms (4) were the most popular chemical blowing agents.

Early attempts to produce open-cell sponge by means of physical blowing agents (eg, alcohol, benzene, and other volatile liquids) met with limited success (5). Eventually, blowing techniques which utilize volatile liquids, either aliphatic hydrocarbons or halogenated hydrocarbons, were perfected; these have attained considerable importance in the manufacture of cellular thermoplastic structures.

Parallel to the development of atmospherically blown sponge, experimental work was carried out with the aim of producing closed-cell rubber by gassing with elemental nitrogen under high pressure. In the early 1930s the Rubatex process (6), based on patents of Pfleumer (7), Marshall (8), Denton (9), and others (10), became commercially well established. Between 1930 and 1950 large quantities of expanded rubber were produced by the Rubatex and similar processes throughout the world. In the last fifteen years the availability of efficient and easily handled organic blowing agents has made the Rubatex process virtually obsolete.

Diazoaminobenzene (DAB), or 1,3-diphenyltriazene, was the first commercially available organic blowing agent. Introduced as Unicel in 1940 by E. I. du Pont de Nemours & Co., Inc. (11), the compound was found extremely useful despite its toxicity and staining properties. For the first time it was possible to make cellular polymers with closed cells by conventional compounding and processing methods (12). As soon as the advantages derived from the use of diazoaminobenzene became apparent, an intensive search began for better organic blowing agents. In the early 1940s, a group of nonstaining aliphatic compounds, the azonitriles, was placed on the market (13), and of these, 2,2'-azobisisobutyronitrile was used on a large scale in the production of flexible and rigid poly(vinyl chloride) compounds during World War

II. Later, 2,2′-azobisisobutyronitrile, due to the toxicity of its residue, was abandoned in favor of nontoxic organic blowing agents. Neither the azonitriles nor the later-suggested derivatives of azodicarboxylic acid (14) could satisfy the need for a versatile, inexpensive blowing agent that would make the chemical blowing method competitive with the Rubatex process. The breakthrough came in 1946 with the introduction of dinitrosopentamethylenetetramine, one of the dinitrosoamines suggested earlier by Briggs and Scharff (15).

In the past forty years over a thousand chemicals have been suggested as blowing agents for high polymers. Some of these enjoyed a short period of commercial acceptance but were later replaced by better products; many others never reached full-scale industrial application, while yet others remained nothing but laboratory curiosities. Today no more than ten chemically different blowing agents are effectively used throughout the world. Presently, the main development effort in this field is directed toward extending the temperature spectrum of the chemical blowing agents by providing compounds with either higher or lower decomposition temperatures than already attainable.

Physical Blowing Agents

The scope of this article is limited to those physical blowing agents which develop a cellular structure by passing from a liquid to a gaseous phase during the blowing operation. These compounds are liquids with boiling points ranging from room temperature to 110°C. Ideally, they should be odorless, nontoxic, noncorrosive, and nonflammable. At low temperatures, the liquids may have some swelling effect on the polymer to be expanded, or it may be desirable that they be soluble in the monomer, but they must possess no solvating power or otherwise affect the physical and chemical properties of the polymer. In the gaseous state, the physical blowing agents must be thermally stable and chemically inert at the temperature employed in the blowing process. The efficiency of physical blowing agents depends upon a complete vaporization of the compound and is directly related to the ratio of the volume occupied by equal weights of the vapor and the liquid. From the standpoint of the effective utilization of the blowing agent, a high specific gravity combined with a low molecular weight is most desirable.

The change from the liquid to the gaseous state is a reversible and endothermic process. When the expanded polymer is cooled, a condensation of the physical blowing agent does not occur, inasmuch as the vapor is either under reduced pressure or diluted with air. The heat of vaporization can be utilized to control the temperature of the expanding polymer as the latter undergoes a chain extension or crosslinking. This permits the preparation of large cellular bodies without the danger of thermal degradation of the polymer. The addition of nucleating agents (eg, silica, silicates, sulfides) which serve as sites of bubble formation facilitates the development of small and uniform vapor-filled cells (16). Furthermore, chemical blowing agents, eg, a bicarbonate–acid system, can be used in conjunction with volatile liquids (17) to develop low-density cellular polymers.

Physical blowing agents are efficient and inexpensive gas-forming compounds but, in general, their use requires specialized equipment designed specifically for a predetermined blowing operation. The most widely used physical blowing agents are the aliphatic hydrocarbons, as well as the chloro- and fluoro-derivatives of aliphatic hydrocarbons. Of lesser importance are low-boiling alcohols (18), ethers (19),

Table 1. Properties of Physical Blowing Agents

Blowing agent	Mol wt[a]	d[25],[a] g/ml	Bp, °C[a]	Heat of vaporization,[a,b] cal (15°)/g	Blowing efficiency[c] At bp	At 100°C
pentanes						
n-pentane	72.15	0.616[30]	36.1	86.0	216	261
2-methylbutane	72.15	0.615	27.8	81.5[25]	210	261
2,2-dimethylpropane	72.15	0.613	9.5		196	260
1-pentene	70.15	0.641[20]	30.0		227	280
cyclopentane	70.15	0.740	49.2	99.6[25]	279	323
hexanes						
n-hexane	86.17	0.655	68.7	80.4[60]	212	232
2-methylpentane	86.17	0.653[15]	60.2	76.5	207	232
3-methylpentane	86.17	0.660	63.3		211	234
2,3-dimethylbutane	86.17	0.657	58.0	75.0	207	233
2,2-dimethylbutane	86.17	0.645	49.7	73.8	204	229
1-hexene	84.17	0.669	63.5		219	243
cyclohexane	84.17	0.774	80.8	94.8[25]	266	281
heptanes						
n-heptane	100.20	0.679	98.4	77.0[90]	206	207
2-methylhexane	100.20	0.674	90.0		200	206
2,2-dimethylpentane	100.20	0.670	79.2	77.3[25]	193	204
2,3-dimethylpentane	100.20	0.691	89.7	81.7[25]	205	211
2,4-dimethylpentane	100.20	0.668	80.6	78.4[25]	193	204
3,3-dimethylpentane	100.20	0.689	86.0		202	210
3-ethylpentane	100.20	0.694	93.4		204	212
2,2,3-triethylbutane	100.20	0.686	80.8	69.0	198	209
1-heptene	98.20	0.693	93.2		212	216
benzene	78.11	0.874	80.1	94.1	324	342
toluene	92.13	0.862	110.6	98.6[25]	294	286
dichloromethane	84.94	1.325	40.0		404	482
trichloromethane	119.39	1.489	61.2	66.7[20]	342	382
trichloroethylene	131.40	1.466	87.2		330	342
tetrachloromethane	153.84	1.584	76.7	46.6	296	316
1,2-dichloroethane	98.97	1.245	83.5	77.3[82.2]	370	388
trichlorofluoromethane	137.38	1.476	23.8	43.5	261	329
1,1,2-trichlorotrifluoroethane	187.39	1.565	47.6	35.1	219	255
methyl alcohol	32.04	0.787	64.6	263.0	679	752
ethyl alcohol	46.07	0.785	78.3	204.0[70]	491	521
isopropyl alcohol	60.09	0.780	82.3	175.6[20]	378	397
ethyl ether	74.12	0.708	34.5	89.8[30]	240	292
isopropyl ether	102.16	0.725	67.5	68.2	198	217
acetone	58.08	0.785	56.2	125.3	365	413
methyl ethyl ketone	72.10	0.810	79.6	103.4	324	344

[a] Data taken from Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, 1950, except that data for isopropyl ether is from Fife and Reid, *Ind. Eng. Chem.* **22**, 513 (1930).

[b] At the boiling point, unless otherwise indicated.

[c] Data computed according to the formula

$$\frac{22,400}{\text{mol wt}} \times (\text{density at } 25°C) \times \frac{(273 + t)}{273}$$

where t = boiling point in °C for the next to the last column and 100°C for the last column. In the first approximation vapors were treated as ideal gases.

ketones (20), and aromatic hydrocarbons (18,20). The physical properties of a number of selected physical blowing agents are given in Table 1.

Aliphatic Hydrocarbons. The main source of liquid aliphatic hydrocarbons are low-boiling fractions of petroleum, variously called "petroleum ether," "ligroin," or "light spirits." The low-boiling solvents contain mainly isomers of pentane, hexane, and heptane, and are available in distillation ranges closely corresponding to the boiling points of the various hydrocarbon isomers. These inexpensive liquids possess a high blowing efficiency and a comparatively low order of toxicity. Their value as blowing agents for polymers is limited by the high degree of flammability. The low-boiling pentanes are used extensively in production of expanded polystyrene (21).

Halogenated Aliphatic Hydrocarbons. The main advantage of chlorinated hydrocarbons is their nonflammability. Because of this property, these materials can be used as blowing agents in making fire-resistant cellular polymers. Chlorinated hydrocarbon blowing agents are more expensive than aliphatic hydrocarbons and present a serious toxicity problem in handling. Among the most commonly used compounds of this group are methylene chloride and tri- and perchlorethylene. Methylene chloride has been used for manufacturing flame-resistant cellular polystyrene, and the chlorinated ethylenes have been suggested as auxiliary blowing agents in making cellular poly(vinyl chloride) (22) and epoxy resins (18).

Fluorinated aliphatic hydrocarbons combine several desirable properties which make these organic liquids ideally suited for use as blowing agents. Among their most significant characteristics are nonflammability, an extremely low level of toxicity, excellent thermal and chemical stability, low thermal conductivity, and good dielectric properties. The high density of fluorocarbon liquids contributes to a favorable blowing efficiency. Of the many commercially available aliphatic fluorocarbons, only two of the common ones are liquid at room temperature—trichlorofluoromethane (available as Freon 11, Du Pont; Genetron 11, Allied Chemical; Isotron 11, Pennsalt Chemicals; and Ucon Propellant 11, Union Carbide Chemicals) and 1,1,2-trichlorotrifluoroethane (available as Freon 113, Du Pont; Genetron 112, Allied Chemical; and Ucon Propellant 113, Union Carbide Chemicals). Both products are presently used on a large scale as blowing agents for flexible and rigid polyurethan foam (23). Their use has been suggested in the preparation of cellular structures based on polyolefin resins (24), poly(vinyl chloride) compositions (25), epoxy resins (26), and phenol- and urea-formaldehyde resins (27).

Chemical Blowing Agents

Chemical blowing agents (28) decompose upon heating with liberation of gaseous products. This is usually an irreversible, exothermic reaction which occurs over a definite and short temperature range. Certain compounds such as bicarbonates, which decompose through thermal dissociation, evolve gas in a reversible and endothermic reaction.

The choice of a chemical blowing agent is dependent upon and limited by its rate of decomposition at elevated temperatures. A rapid rate of decomposition is desirable, but a violent breakdown of the compound must be avoided. The rate of decomposition should not be affected by pressure if the compound is to be used in the expansion process involving high pressures. To be useful commercially, the blowing agent must be stable over an extended period of time at temperatures encountered under ordinary storage conditions.

Chemical blowing agents preferably decompose with liberation of nitrogen, but other gaseous products such as carbon dioxide, carbon monoxide, and hydrogen are frequently encountered. Corrosive gases (eg, nitrogen dioxide, sulfur dioxide, and hydrogen chloride) should be absent from the decomposition products. Also, the generated gas should be virtually insoluble in the polymer.

To obtain homogeneous distribution in the polymer, the blowing agent should be either easily dispersible by conventional methods of mixing, or should be soluble, in the polymer. Furthermore, it is important that the blowing agent and its decomposition products exert no adverse effects on the physical and chemical properties of the polymer. For example, the rate of fusion (ie, intimate blending of resin and plasticizer under the influence of heat) or crosslinking should not be impaired, the electrical properties should not deteriorate, and the thermal and chemical resistance of the polymer should not be decreased by the presence of the residue.
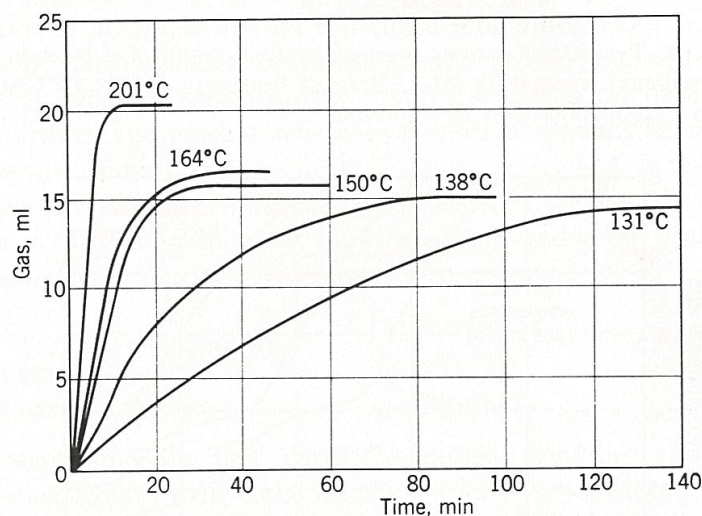

Fig. 1. Gas development curves of dinitrosopentamethylenetetramine (30).
Courtesy *Plastics Progress*.

The commercial acceptance of a chemical blowing agent quite often hinges on the properties of the residue. Ideally, the residue should be colorless, nonstaining, nondiscoloring, nonflammable, compatible with the polymer, and should impart no objectionable odor. It is also essential that both the blowing agent and the residue be nontoxic and relatively harmless to the skin.

The efficiency of chemical blowing agents can be measured by the quantity of gas given off upon decomposition and is usually expressed as ml/g of blowing agent under given conditions. An inexpensive blowing agent is not necessarily the most economical if its gas yield is low. A gas yield based on unit cost better characterizes the efficiency of a blowing agent than does a gas yield computed on the basis of unit weight.

The major advantage derived from the use of chemical blowing agents is their ease of handling and their adaptability to processes requiring conventional equipment.

Testing Methods. The thermal behavior of chemical blowing agents has been a subject of many investigations, and numerous methods have been proposed for the determination of the decomposition rate, temperature, and gas yield.
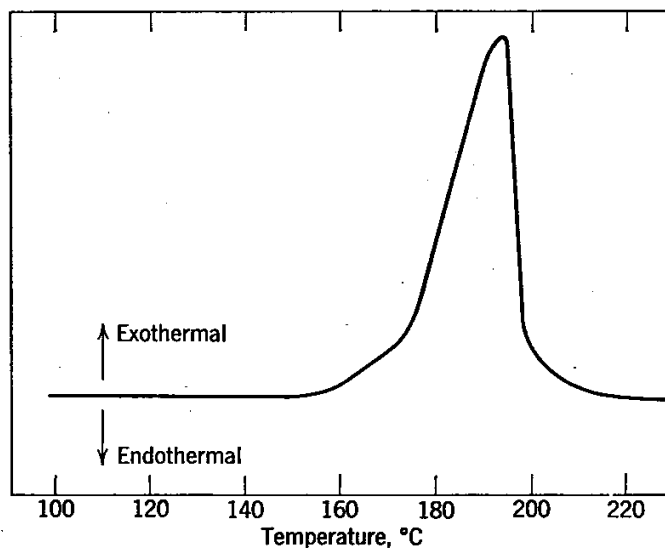
Fig. 2. Typical differential thermal analysis graph of 4,4'-oxybis-(benzenesulfonyl hydrazide) (31). Rate of heating: approx 10°C/min; reference: Al_2O_3. Courtesy *SPE Journal.*
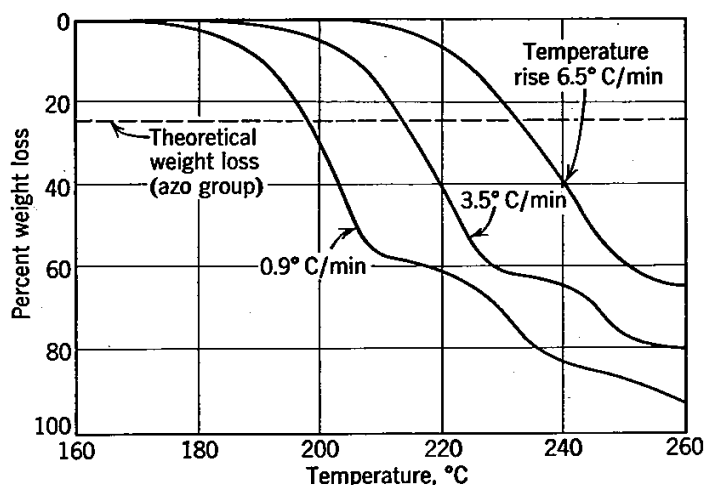
Fig. 3. Typical thermogravimetric analysis graph of azodicarbonamide (31).
Courtesy *SPE Journal.*

To compare the efficiency of blowing agents, Cooper (29) used an oil-heated, high-pressure gas bomb connected with a manometer which allowed the observation of pressure rise as the decomposition of the agent progressed. In another method, the relative performance of blowing agents and their behavior in various liquids was studied by measuring the volume of the evolved gas as a function of the heating time at several temperature levels (30). Typical results obtained by this method are shown in Figure 1.

In recent years differential thermal analysis (qv) and thermogravimetric analysis (qv) have been employed to investigate blowing agents (31). Differential thermal analysis permits the determination of the exotherm which is generated at the decomposition point of the blowing agent. A typical differential thermal analysis curve of the decomposition of a blowing agent is illustrated in Figure 2. Using thermogravimetric analysis, the decomposition of a blowing agent can be followed by measuring

the weight loss of a sample heated at a constant rate. Figure 3 depicts results that can be obtained with thermogravimetric analysis.

The American Society for Testing and Materials in cooperation with the Society of the Plastics Industry has issued a tentative method, ASTM D 1715-60T, for determination of the total gas volume evolved from chemical blowing agents. This method is not applicable to measuring the rate of decomposition.

In all methods previously discussed, the rate of decomposition of the blowing agent is determined under environmental and thermal conditions significantly different from those encountered in the preparation of cellular polymers. Meaningful information on the thermal behavior of blowing agents in polymers can be obtained when their performance is compared in a particular polymer system under controlled thermal conditions. For instance, in the absence of a crosslinking or stiffening effect of the decomposition products, the degree of expansion of the polymer is directly related to the quantity of gas given off by the blowing agent at a constant time–temperature cycle (32), provided no gas is lost by cell rupture or diffusion.

Economics. No data are available on the production and consumption of chemical blowing agents. Authoritative market statistics on blowing agents have never been published, and market estimates of various blowing agent manufacturers are closely guarded secrets.

In 1960, the U.S. Tariff Commission published, for the last time, figures on production and sales of organic chemical blowing agents under the heading of "Rubber Processing Chemicals." The following figures were reported:

	Production, lb	*Sales, lb*
Blowing agents, cyclic	3,650,000	3,416,000
Blowing agents, acyclic	688,000	457,000

At the present time, the U.S. Tariff Commission combines the statistical information on blowing agents with those on other rubber processing materials, eg, peptizers, lubricants, etc. The five blowing agents included in the survey are 4,4'-oxybis-(benzenesulfonyl hydrazide), N,N'-dimethyldinitrosoterephthalamide, dinitrosopentamethylenetetramine, azobisformamide, and a urea–biuret mixture.
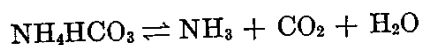
Carbonates

Ammonium Carbonate. Ammonium carbonate is a white, crystalline powder with a strong ammoniacal odor. It may be prepared by reacting carbon dioxide with ammonia in the presence of water. The commercially available product is actually a mixture (or a double salt) of ammonium bicarbonate and ammonium carbamate (NH_2-$CONH_4$). When exposed to air, the crystals of ammonium carbonate liberate ammonia and water and are transformed into a moist ammonium bicarbonate powder. The thermal dissociation of ammonium carbonate starts at 30°C and the reaction proceeds quite vigorously at 55–60°C.

The compound is a "total" blowing agent in that it decomposes without leaving a residue. At 100°C the gas yield is 980 ml (STP)/g, one of the highest of all chemical blowing agents. The usefulness of ammonium carbonate as a blowing agent is severely limited by its poor storage stability, the indefinite composition of the commercial product, the objectionable ammonia odor, and the difficulty with which the material can be dispersed in high polymers. The storage stability of ammonium carbonate can be improved, according to patent literature, by blending it with magnesium carbonate

(33), zinc oxide (34), or alkylamines (35). Pastes consisting of the blowing agent and processing oils have better stability as well as improved dispersibility (36). Ammonium carbonate has been used in the production of sponge rubber (37); however, it has been displaced by the more stable sodium bicarbonate. It has also been proposed as an auxiliary blowing agent in the preparation of polyurethan foam (38), as an additive to dinitrosopentamethylenetetramine for making poly(vinyl chloride) foam (39), and as a blowing agent for urea–formaldehyde glues (40) and chlorosulfonated polyolefin compounds (41). The 1963 price of ammonium carbonate (USP grade) was 23.5–24.5¢/lb.

Ammonium Bicarbonate. Ammonium bicarbonate is more stable and easier to obtain in pure form than ammonium carbonate. Commercially, ammonium bicarbonate is prepared by passing carbon dioxide through an aqueous solution of ammonia. Under atmospheric pressure and in the absence of moisture, the salt decomposes slowly at 60°C yielding ammonia, carbon dioxide, and water.

$$NH_4HCO_3 \rightleftharpoons NH_3 + CO_2 + H_2O$$

The gas yield is 850 ml (STP)/g assuming water to be available as vapor. In 1963 ammonium bicarbonate sold at 7.5–8.5¢/lb. It is therefore more economical as a blowing agent than ammonium carbonate. Moisture accelerates the dissociation of the salt, and high pressure suppresses the formation of the gaseous decomposition products.

Ammonium bicarbonate suffers from the same disadvantages as the carbonate and can be used in the same applications.

Sodium Bicarbonate. Among the inorganic blowing agents only sodium bicarbonate has remained in use over the years, although the introduction of organic blowing agents greatly diminished its importance in the manufacture of cellular polymers.

Sodium bicarbonate is an odorless nontoxic white powder (specific gravity 2.20), which is obtained as an intermediate in the manufacture of soda ash by the Solvay process, or by reacting sodium carbonate solution with carbon dioxide. The salt decomposes slowly at approximately 100°C with an attendant evolution of carbon dioxide; at 140°C the decomposition proceeds at a rapid but still controllable rate.

$$2 NaHCO_3 \rightleftharpoons Na_2CO_3 + CO_2 + H_2O$$
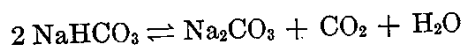
Assuming water to be available as vapor, the total gas yield is 267 ml (STP)/g, which, combined with a low price (2.5¢/lb in 1963), makes sodium bicarbonate the most economical chemical blowing agent. However, the residue of this decomposition is strongly alkaline and thus objectionable in many applications. Also, the degree of dissociation of sodium bicarbonate decreases rapidly with increased pressure and, therefore, the blowing agent cannot be used effectively in high-pressure expansion processes.

The storage stability of sodium bicarbonate is adequate but the material tends to pick up moisture and to cake badly. However, finely ground sodium bicarbonate remains free-flowing if conditioned with additives such as magnesium stearate (Ansulblo, Ansul Chemical Co.; now withdrawn) (42). In blowing polymers, the efficiency of sodium bicarbonate is significantly lower than indicated by the gas yield. This is due to the rapid rate of diffusion of carbon dioxide from polymers, and to the poor dispersibility of the salt in elastomers and plastics. A paste of finely ground sodium

bicarbonate (particle size less than 15 μ) in light process oil with lecithin as an emulsifier (43) possesses improved dispersibility and can be mixed easily with elastomers. This product, Unicel S (Du Pont), has enjoyed commercial acceptance in the production of cellular rubber goods. Surface-active agents can also improve the dispersibility and efficiency of sodium bicarbonate paste (44). A coprecipitated masterbatch of sodium bicarbonate-containing rubber has been claimed (45) to facilitate the dispersion of the blowing agent in rubber compositions.

In the thermal decomposition of sodium bicarbonate, only half of the theoretically available carbon dioxide in the molecule is evolved. A total decomposition of the bicarbonate can be achieved by the use of acidic materials. In practice, weak acids are used in conjunction with sodium bicarbonate to obtain a higher gas yield from the blowing agent. For expansion of rubber, sodium bicarbonate is activated with stearic acid, oleic acid, or cottonseed oil acid. In thermosetting resins, the acidic curing catalyst also acts as an activator for the blowing agent.

Sodium bicarbonate has been extensively employed in the manufacture of open-cell rubber sponge (46) based on all types of natural and synthetic elastomers. Phenolic resin foams can be prepared by reacting the bicarbonate with an acid hardener (47), and this process has become commercially important. Other polymers that can be expanded with sodium bicarbonate are natural and synthetic latexes (48), polyethylene (49), alkyd resins (50), poly(vinyl chloride) (51), epoxy resins (52), polyamides (53), and acrylic resins (54).

Organic Carbon Dioxide-Generating Chemicals. Ethylene carbonate (55) (1) is an example of organic blowing agents which decompose in polymers in the temperature range of 120–200°C with the liberation of carbon dioxide (56). The ad-

$$O=C{<}^{OCH_2}_{OCH_2}|$$

(1)
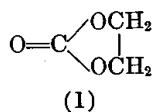
vantage claimed for this compound is its compatibility with a wide variety of polymers, which facilitates dispersion and thus leads to the formation of very fine cells.

Nitrites

Ammonium Nitrite. Ammonium nitrite, through its thermal decomposition, offers a convenient source of elemental nitrogen. Prior to the introduction of organic blowing agents, this product had been suggested as an expanding agent for pressure-blown cellular rubber (57).

In practice, ammonium nitrite is prepared in situ by incorporating into the rubber mix equimolar quantities of ammonium chloride and sodium nitrite. During the heating of the rubber, nitrogen is liberated.

$$NH_4Cl + NaNO_2 \rightarrow N_2 + 2 H_2O + NaCl$$
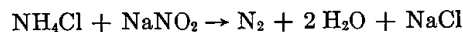
Unlike the thermal dissociation of carbonates, the decomposition of ammonium nitrite is an irreversible, exothermic reaction which proceeds independently of external pressure. The reaction produces nitrogen, but small quantities of nitric oxides which have a cure-accelerating effect and which cause corrosion of molds and other processing equipment are also generated (58). Small quantities of water and polyhydric alcohols (59) accelerate the evolution of gas. The hygroscopic sodium nitrite introduces enough moisture into the compounded polymer to initiate the reaction as soon

as it comes into contact with ammonium chloride. End results are unpredictable. In common with other inorganic blowing agents, both sodium nitrite and ammonium chloride are difficult to disperse in polymers.

At the present time, ammonium chloride–sodium nitrite pills are used as an inflating agent during the curing of hollow rubber goods (eg, children's balls).

To overcome some of the disadvantages of ammonium nitrite, stabilized complexes of this compound have been proposed (60); however, in 1963 they had not been commercially exploited.

Organic Nitrites. Various organic nitrites have been considered for use as blowing agents.

Alkylamine nitrites ($RNH_2.HNO_2$) represent a group of organic nitrogen-releasing blowing agents which have been suggested for use in rubber (61) and in poly(vinyl chloride) (62). The compounds decompose with evolution of nitrogen and water.

$$RNH_2.HNO_2 \rightarrow ROH + N_2 + H_2O$$

tert-Butylamine nitrite, which was test marketed in the United States in 1955 as Blowing Agent X-950 (Rohm & Haas), decomposes at around 120°C and yields 374 ml (STP)/g (considering the evolved water as vapor).

Amidine nitrites ($R—C(:NH)—NH_2.HNO_2$), in particular guanidine nitrite (dec 99–110°C), guanylurea nitrite (dec 139°C), and acetamidine nitrite (dec 155–160°C), have been claimed in the patent literature as blowing agents for rubber and plastics (63), but have not been used for this purpose commercially.

Hydrides and Peroxides

Alkali Borohydrides. In recent years borohydrides, in particular potassium and sodium borohydrides, have been promoted as blowing agents. These compounds are convenient sources of hydrogen.

The rate of hydrolysis of alkali borohydrides is governed by the hydrogen ion concentration and increases rapidly with decreasing pH. In nonaqueous systems, acidic compounds (eg, phthalic anhydride, stearic acid, or glycine) are added along with a small quantity of water. Under these conditions the decomposition of the borohydrides proceeds rapidly with the evolution of hydrogen. This reaction is also catalyzed by certain metallic salts, notably those of iron, cobalt, or nickel.

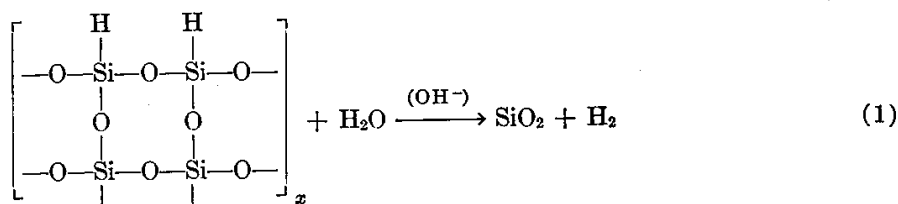$$MBH_4 + 2 H_2O \xrightarrow{\;(H^+)\;} MBO_2 + 4 H_2$$
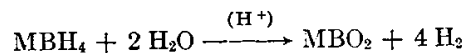
As a result of the decomposition of the blowing agent within the polymer matrix, hydrogen is entrapped in the cells; however, it diffuses rapidly and is replaced by air. This may create explosion hazards unless the concentration of hydrogen in and around processing equipment is kept below 4%.

Potassium borohydride is a white crystalline solid which is nonhygroscopic under normal storage conditions. In air, it ignites from a free flame and burns quietly. The compound is readily soluble in water. Its rate of decomposition in an alkaline solution is very slow below 100°C. Under acidic conditions and/or at elevated temperatures, potassium borohydride decomposes rapidly, yielding 1600 ml (STP) hydrogen/g.

Sodium borohydride is a hygroscopic solid which decomposes slowly in moist air. In acidic media the compound generates 2370 ml hydrogen (STP)/g.

Alkali borohydrides have been proposed as blowing agents for several polymers in aqueous systems—rubber latex (64), poly(vinyl acetate), poly(vinyl alcohol), and melamine–formaldehyde resins (65). Poly(vinyl chloride) plastisols are expanded at room temperature with borohydrides in the presence of water and organic acids (66); the reaction can be delayed by the addition of isocyanates (67). A blend containing 5% potassium borohydride extended with clay was offered commercially (Hydri-Foam, Metal Hydrides, Inc., Beverly, Mass.) for blowing natural and synthetic elastomers in the presence of stearic acid (68), but the product failed in production trials (69) and was withdrawn from the market. In 1963 sodium borohydride sold at $14.00/lb and potassium borohydride at $17.00/lb. The high price, the moisture sensitivity of borohydrides, and the fire and explosion hazards of the hydrogen generated limit the industrial acceptance of these compounds as blowing agents.

Silicon Oxyhydride. Silicon oxyhydride is a white, storage-stable, free-flowing powder; it liberates hydrogen either on heating (350°C) or under the influence of bases (eq. 1).

$$\begin{bmatrix} & \overset{\displaystyle H}{\underset{\displaystyle |}{|}} & & \overset{\displaystyle H}{\underset{\displaystyle |}{|}} & \\ -O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O- \\ & O & & O & \\ -O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O- \\ & | & & | & \end{bmatrix}_x + H_2O \xrightarrow{(OH^-)} SiO_2 + H_2 \qquad (1)$$

The blowing agent is capable of generating 423 ml hydrogen (STP)/g and leaves as a residue silica filler which imparts some reinforcement to elastomers. Silicon oxyhydride has been suggested as an expanding agent for synthetic elastomers, mainly silicone rubbers (70).

Peroxides. Among the oxygen-releasing blowing agents, *hydrogen peroxide* is of particular commercial importance for foaming of rubber latex. In the Talalay process (71), use is made of the ability of minute quantities of the enzyme catalase to decompose hydrogen peroxide rapidly at room temperature. Latex foam prepared by the Talalay process has a lower apparent density and a more uniform cell structure than foams obtained by the mechanical foaming method of Dunlop (72). Similar results are claimed for a foaming method utilizing hydrogen peroxide in conjunction with polyamines (73). Latex foam can also be successfully produced with *urea peroxide* as blowing agent (74).

Oxalic Acid Derivatives

Oxalic acid derivatives comprise a group of carbon dioxide-generating blowing agents. Among the salts, *ferrous oxalate* (dec 160°C) has been specifically recommended for the blowing of rubber compounds (75). Of greater practical importance have been the oxalates of weak organic bases. Oxalates of urea, methylurea, biuret, dicyandiamide, and melamine, or physical mixtures of oxalic acid and the organic base in an equimolar ratio, were found (76) to be efficient blowing agents for polymeric materials.

Urea oxalate has been offered commercially as Hucel (Hubron Rubber Chemicals, Ltd., Manchester, England) for use in the manufacture of rubber sponge (77). This salt can be prepared from aqueous solutions of the urea and oxalic acid in the presence of sodium alginate, casein, or oil emulsion, all of which reduce the crystal growth of the precipitated urea oxalate. Urea oxalate is relatively stable up to 130°C, but

decomposes rapidly at 145°C. The gas yield is 140 ml (STP)/g. The gaseous phase consists mainly of carbon dioxide and carbon monoxide in the ratio 3.5:1, but some nitrogen, ammonia, and water vapor are also present. Urea oxalate produces odorless, nonstaining rubber sponge with small and uniform cells. In conjunction with sodium bicarbonate, it has been used in the production of soft cellular-rubber shoe soling applied directly to canvas uppers.
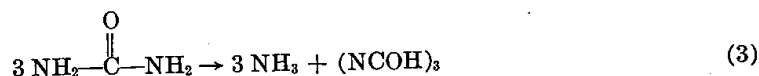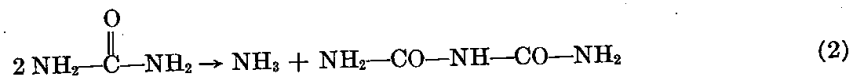
In addition to urea oxalate, blends of urea and oxalic acid in molar ratios varying from 1:1 to 5:1 have been considered useful as blowing agents for rubber and plastics (78).

1,1'-Dithiodiformamidine (bis(methyliminoamino)disulfide oxalate), NH₂C-(:NH)—S—S—C(:NH)NH₂(COOH)₂, liberates carbon dioxide and carbon monoxide at 120–125°C. It can be easily prepared by the oxidation of thiourea with hydrogen peroxide in the presence of oxalic acid. Its use as a blowing agent for rubber was patented as early as 1937 (79), but it has not been found attractive commercially. Rubber sponge expanded with this oxalate displays an unpleasant odor.

Of more recent interest is the claim (80) that *oxamic acid*, H_2N—CO—COOH, (dec 214°C) and its methyl and ethyl esters are useful in the expansion of polyamides having softening points between 170 and 220°C.

Urea and Related Compounds

Urea. Urea is a white, crystalline, highly hygroscopic material (sp gr 1.34) with a melting point of 132.7°C. When slowly heated beyond the melting point, it decomposes (eq. 2) with the evolution of ammonia, leaving biuret as the residue. When heated rapidly to a temperature above 150°C, cyanic acid, which trimerizes to cyanuric acid, is formed (eq. 3).

$$2\,NH_2\overset{O}{\underset{\|}{C}}NH_2 \rightarrow NH_3 + NH_2\text{—}CO\text{—}NH\text{—}CO\text{—}NH_2 \tag{2}$$

$$3\,NH_2\overset{O}{\underset{\|}{C}}NH_2 \rightarrow 3\,NH_3 + (NCOH)_3 \tag{3}$$

The first decomposition route generates 187 ml (STP) ammonia/g; in the second decomposition reaction twice as much ammonia is liberated. Despite this high gas yield, urea is used only occasionally as a blowing agent for rubber (81). However, it plays an important role in the manufacture of cellular rubber as an activator for dinitrosoamine-type blowing agents (82) and as a secondary cure accelerator in conjunction with thiazole- and thiuram-type accelerators. Because of the difficulty with which the crystalline material is dispersed in elastomers, finely ground, non-caking urea products have generally been employed (RIA NC, National Polychemicals; BIK, Naugatuck Chemical Division, U.S. Rubber Co.). Also, a urea–metal salt complex (mp 100–115°C) (83) is being offered for the same application (Aktone, J. M. Huber Co.). The 1963 prices of the non-caking grades of ground urea were 20–22¢/lb; the urea complex sold at 21.25–23.25¢/lb.

Biuret. Biuret (dec 192–193°C) has been claimed as a blowing agent for elastomers (84), but only mixtures of urea and biuret are commercially exploited. Heating an equimolar blend of these two compounds (85) liberates 275 ml (STP) ammonia/g.

$$NH_2\text{—}CO\text{—}NH\text{—}CO\text{—}NH_2 + NH_2\text{—}CO\text{—}NH_2 \rightarrow 2\,NH_3 + (NCOH)_3$$
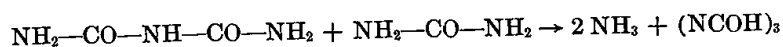
The commercial product (Blowing Agent 81105, Sherwin-Williams) is a noncaking powder (sp gr 1.45) which disperses fairly well in rubber. It produces odorless, non-staining, and nondiscoloring cellular products and is recommended for use either alone or in combination with other blowing agents such as sodium bicarbonate or dinitrosoamines. The residue, cyanuric acid, has no deleterious effect on rubber and, because it is virtually insoluble in water, cannot be leached when the cellular product is immersed in water. The efficiency of the urea–biuret blend at the usual blowing temperatures is higher than that of either component. In 1963, the commercial product was offered at 32–35¢/lb.

Aminoguanidine bicarbonate (NH_2—NH—C(:NH)—NH_2.H_2CO_3) and *amino-guanyl urea* (NH_2—NH—C(:NH)—NH—CO—NH_2) decompose with the evolution of ammonia and nitrogen (also carbon dioxide from the bicarbonate). Both chemicals have been considered as blowing agents for rubber (86,87), but their commercial application is economically impractical.

The *N-nitro derivatives of urea* and related organic bases have been described in the patent literature as blowing agents for plastics (88). The decomposition temperatures of these compounds range from as low as 120°C (*N*-nitro-*N'*-cyclohexylurea) to as high as 230°C (*N*-nitroguanidine). The thermal decomposition of the *N*-nitro compounds leads to the liberation of gases containing nitrous oxide and carbon dioxide as the main components. Most of the compounds of this group are odorless, color-less, easily dispersible solids which can be conveniently obtained by the nitration of the corresponding organic bases. It is claimed that the preparation and handling of these nitro compounds present no explosion hazards, but an American source (89) describes the parent compound, *N*-nitrourea, as highly sensitive to shock and dangerous when exposed to heat and flame.

N-Nitrourea (NH_2—CO—NH—NO_2) (Genitron N, Whiffen & Sons, Ltd., Lough-borough, England) decomposes in air at 158–159°C giving off nitrous oxide, carbon dioxide, ammonia, and water vapor (90). When decomposed in paraffin at 129°C, the compound generates 380 ml gas/gram (91). It may be used as a blowing agent in the production of cellular polymers, both thermoplastic and thermosetting (92). The decomposition rate of *N*-nitrourea can be accelerated by the addition of organic bases (eg, hydrazine, morpholine, or methylamine) with which it forms salts decomposing at temperatures below 100°C (93). The activation of *N*-nitrourea with alkyl-amines has been applied to the preparation of expanded potting compounds based on epoxy resins (91). *N*-Nitroguanidine (NH_2—C(:NH)—NH—NO_2) has been suggested as a blowing agent for high-melting polyolefins, in particular for linear polyethylene and polypropylene (94).

Azo Compounds

Aromatic Azo Compounds. Among the aromatic azo compounds, the triazenes have received the greatest attention and use as blowing agents. Other compounds that have been proposed as blowing agents are arylazosulfones (106), arylazotriaryl-methanes (107) (also the hydrazo compound (108)), and diazoethers (109). See also Azo catalysts.

Diazoaminobenzene (1,3-diphenyltriazene, $C_6H_5NHN=NC_6H_5$), the first com-mercially available organic nitrogen-releasing blowing agent, can be obtained by diazotization of aniline, followed by a coupling with the same base in a solution buf-fered with sodium acetate (95). The pure compound forms needlelike, golden-yellow

crystals (sp gr 1.17), which melt with decomposition at 98°C. The commercial product, DAB (National Aniline Division, Allied Chemical Corp.), is a brown-colored, crystalline powder with a characteristic aromatic odor. It decomposes between 90 and 95°C (96), and liberates 113–115 ml nitrogen (STP)/g. It disperses easily since it is soluble in elastomers up to 8% in highly plasticized rubber stocks. Larger quantities of the blowing agent tend to bloom from the uncured rubber compositions, but no blooming occurs from vulcanizates containing as much as 15% diazoaminobenzene. In the presence of aldehyde–amine type accelerators, diazoaminobenzene has no effect on the rate of vulcanization, a property which is of considerable importance in the manufacture of cellular hard rubber. The blowing agent imparts an intense orange discoloration, which precludes its use in light-colored goods. Cellular products made with diazoaminobenzene stain many types of substrates, including paper, cloth, rubber, and organic coatings. This blowing agent and cellular polymers made with it may cause skin irritation; the use of diazoaminobenzene is therefore restricted to the manufacture of industrial goods. Diazoaminobenzene is an efficient and economical blowing agent which produces expanded products with small, uniform cells. The material has been used in the production of cellular rubber (11,12,29). Its application in poly(vinyl chloride) (97), phenolic resins (98), and rubber–resin blends (99) has also been claimed. The 1963 price was 73¢/lb in ton lots.

Attempts have been made to develop aromatic azo compounds free of the undesirable features of diazoaminobenzene. The elimination of staining properties has been claimed for a group of *sym*-xenyltriazenes (100), of which the 1,3-bis(*o*-xenyl)-triazene (101) is said to be nondiscoloring as well. The latter decomposes at 130–135°C and yields 67 ml nitrogen (STP)/g. More efficient are the diarylpentazadienes (102) of the general structure Ar—N=N—N(R)—N=N—Ar (where R = H, aryl, or alkyl), some of which liberate approximately the same quantity of gas as diazoaminobenzene. Because they are more costly to produce than the latter, pentazadienes have never been used commercially.

Among other triazenes, the substituted mono- and bissulfonyl (103,104) derivatives have been found to be of some interest as blowing agents. In particular, *N*-cyanoalkylsulfonyltriazenes (105) have been considered useful as nonstaining blowing agents with low levels of toxicity. One of these compounds, 1-benzenesulfonyl-3-cyanoethyl-3-phenyltriazene, was test marketed in the United States in 1954–1955 as Cycocel (American Cyanamid), a 40% active blend. It has been withdrawn from the market. The tan-colored product decomposes at 110°C with a gas yield substantially lower than that of diazoaminobenzene. Cellular polymers prepared with this triazene are odorless and nonstaining.

Aliphatic Azo Compounds. Blowing agents of this general chemical type include azonitriles and derivatives of azodicarboxylic acid. See also Azo CATALYSTS.

Azonitriles (13) have an important advantage over diazoaminobenzene in that they permit the production of nonstaining, white, and odorless cellular polymers. The most useful compound of this class is *2,2'-azobis(2-methylpropionitrile)*, better known as 2,2'-azobisisobutyronitrile (110). The compound may be synthesized by reacting acetone and alkali cyanide (or acetone cyanohydrin) with hydrazine sulfate, and oxidizing the resulting hydrazo nitrile with chlorine in an aqueous medium (111). In an alternate method (112), acetone cyanohydrin and ammonia are converted to 2-aminoisobutyronitrile which is then oxidized with an alkali hypochlorite to yield

2,2'-azobisisobutyronitrile. The dry, pure product has a melting point of 105°C. The commercially offered blowing agent (Porofor N, Farbenfabriken Bayer; Genitron AZDN, Whiffen & Sons) melts around 100°C and gives off 136 ml nitrogen (STP)/g. The thermal decomposition of 2,2'-azobisisobutyronitrile has been reviewed recently by Hammond (113). The following compounds have been identified as decomposition products: tetramethylsuccinonitrile (TMSN), isobutyronitrile, methacrylonitrile, and ketenimine. The main constituent of the residue, tetramethylsuccinonitrile, has a high level of oral toxicity (114) (LD_{50} 60 mg/kg body weight). In solution, 2,2'-azobisisobutyronitrile decomposes by first-order kinetics in a wide range of solvents (115) and yields a free radical, 2-cyanopropyl, which can be used as an initiator in vinyl-type polymerizations (116) (see Azo CATALYSTS). A purified form of 2,2'-azobisisobutyronitrile is being offered for this purpose (Vazo, Du Pont; Poly-Zole, National Polychemicals).

2,2'-Azobisisobutyronitrile is a white, fine crystalline powder (sp gr 1.10), readily soluble in elastomers, many conventional solvents (ketones, esters, alcohols, and aromatic hydrocarbons), and vinyl monomers (styrene, vinyl chloride, methyl methacrylate). It is virtually insoluble in water and aliphatic hydrocarbons. The storage stability of the compound is fairly good. At 90°C, 33% of the blowing agent decomposes in an hour; at 40°C, 2.5% in a week. To preserve efficiency, it is preferably stored below 30°C. It is a flammable solid; it can be readily ignited with an open flame and continues to burn vigorously and completely when the source of flame is removed. Dry 2,2'-azobisisobutyronitrile can also be decomposed by a direct blow with a hammer, but no detonation occurs.

This blowing agent has no cure-activating effect on rubber and does not adversely affect the aging properties of cellular vulcanizates. In poly(vinyl chloride) compositions, the residual tetramethylsuccinonitrile acts as a hydrogen chloride acceptor, facilitating the heat stabilization of cellular vinyl compositions expanded with 2,2'-azobisisobutyronitrile.

The main disadvantage of 2,2'-azobisisobutyronitrile is the toxicity of the residue. The health hazards connected with its handling and processing can be minimized by the use of a nondusting, oil-treated form of the blowing agent, and by providing good ventilation of the work area. Vulcanizing presses and expansion and annealing ovens must be equipped with adequate exhaust systems. Expanded products should be washed with warm water to remove from the surface the bloom of the toxic tetramethylsuccinonitrile, which is incompatible with the polymer.

During and shortly after World War II, large quantities of 2,2'-azobisisobutyronitrile found widespread applications in the manufacture of cellular elastomeric, thermoplastic, and thermosetting products (117). Since 1955, however, it has been forced aside in the blowing agent field as better compounds at lower prices became available. Currently, this product is mainly used as a polymerization initiator and only minor quantities go into the expansion of poly(vinyl chloride) and polystyrene (118). In 1963, the polymerization grade cost $1.50/lb.

1,1'-Azobiscyclohexanecarbonitrile, also known as azobis(hexahydrobenzonitrile) or azocyclohexylcyanide (CHDN) (119), is less hazardous to process than 2,2'-azobisisobutyronitrile because the main component of its residue, dicyanodicyclohexyl, possesses a lower level of toxicity than tetramethylsuccinonitrile. This homolog of 2,2'-azobisisobutyronitrile can be obtained by a process similar to that employed for making 2,2'-azobisisobutyronitrile, with the substitution of cyclohexanone for acetone

(111). The pure compound decomposes at 114–115°C, and the commercially offered product (Genitron CHDN, Whiffen & Sons; Porofor 254, Farbenfabriken Bayer) at approximately 105°C. 1,1′-Azobiscyclohexanecarbonitrile decomposes more slowly than 2,2′-azobisisobutyronitrile and theoretically yields only 92 ml nitrogen (STP)/g. In spite of some advantages over 2,2′-azobisisobutyronitrile, 1,1′-azobiscyclohexanecarbonitrile has never become firmly entrenched in the field of blowing agents; it is more expensive and less efficient than the former.

A high gas yield and a nontoxic residue characterize the oxime derivative of 2,2′-azobisisobutyronitrile. *Azobisisobutyramidoxime* (120), obtained by reacting alcoholic solutions of hydroxylamine with 2,2′-azobisisobutyronitrile, is a white crystalline solid decomposing at 148°C. The compound, Genitron AO (Whiffen & Sons), was test marketed in Great Britain in 1955–1956, but was later withdrawn because of its high exotherm.

Among the derivatives of azodicarboxylic acid (14), the diamide is of major interest as a blowing agent for polymers. *Azobisformamide* (ABFA), often called azodicarbonamide, is prepared by reacting hydrazine with an alkali cyanate (121) or urea (122), followed by the oxidation of the resulting hydrazo compound with chlorine (111), chromic acid (123), a nitrate in the presence of a catalyst (salts of copper, cobalt, nickel, iron, and manganese) (124), or sodium chlorate in the presence of ammonium metavanadate (124a). The oxidation step, when carried out under closely controlled conditions, can yield a product of small particle size and narrow size distribution (125).
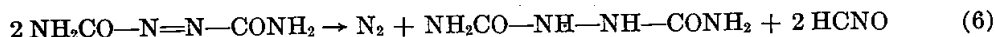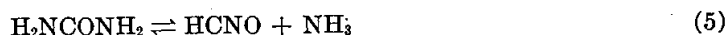
When pure, azobisformamide forms orange-yellow crystals having a melting point of approximately 230°C. The commercial product (Kempore, National Polychemicals; Celogen AZ, Naugatuck Chemical Division, U.S. Rubber; Lucel ADDA, Lucidol Division, Wallace & Tiernan; Azocel, Fairmount Chemical Co.) is, depending upon the particle size, an orange-yellow to pale yellow powder (sp gr 1.65) decomposing in air at 195–205°C. Heated in a plasticizer above 210°C, the blowing agent evolves 220 ml gas (STP)/g, the highest gas volume of all organic blowing agents commercially available in 1963. Although azobisformamide is practically insoluble in common solvents and ester plasticizers, it is dispersed easily by conventional mixing methods in all elastomers and plastics. This blowing agent is slightly soluble in dimethylformamide, and more soluble in dimethyl sulfoxide (4–5 g/100 g solvent at 20°C). Its storage stability is unexcelled. Unlike other known organic blowing agents, azobisformamide does not support combustion and is self-extinguishing.

The thermal decomposition of dry azobisformamide in air yields the following products:

gaseous products	32% by wt
nitrogen	65% by vol
carbon monoxide	32% by vol
carbon dioxide	3% by vol
residue	68% by wt

The composition of the residue varies depending upon the medium in which the blowing agent has been decomposed. In all instances, the following have been identified: hydrazobisformamide (biurea), cyanuric acid, urazole, and, under certain conditions, oxamide. The decomposition mechanism appears to be complex and no theory has been offered to account quantitatively for the presence of all decomposition products.

548 *Blowing Agents*

Reed (126) suggested that the primary decomposition of azobisformamide follows two main routes. In the first, shown in equations 4 and 5, nitrogen and carbon monoxide are liberated. In the second, shown in equation 6, nitrogen is evolved and biurea and cyanic acid are formed. Cyanuric acid and urazole, two constituents of the residue, are formed from cyanic acid and from biurea, respectively.

$$NH_2CO-N=N-CONH_2 \rightarrow N_2 + CO + NH_2CONH_2 \qquad (4)$$

$$H_2NCONH_2 \rightleftharpoons HCNO + NH_3 \qquad (5)$$

$$2\,NH_2CO-N=N-CONH_2 \rightarrow N_2 + NH_2CO-NH-NH-CONH_2 + 2\,HCNO \qquad (6)$$
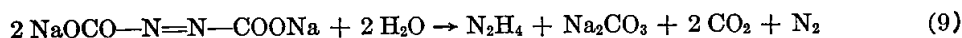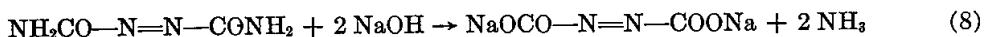
At elevated temperatures and in the presence of water, azobisformamide hydrolyzes with the evolution of nitrogen, carbon dioxide, and ammonia (eq. 7). In a

$$2\,NH_2CO-N=N-CONH_2 + 2\,H_2O \rightarrow$$
$$N_2 + 2\,CO_2 + 2\,NH_3 + NH_2CO-NH-NH-CONH_2 \qquad (7)$$
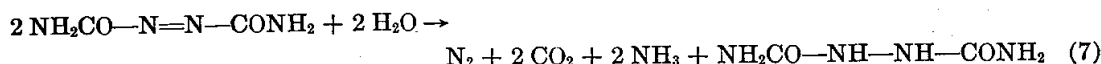
neutral medium, the rate of hydrolysis is slow at temperatures below 100°C, but in the presence of alkali carbonates a rapid decomposition occurs at 100°C. This reaction permits a quantitative determination of azobisformamide by the absorption of the generated ammonia in boric acid.

Cold aqueous alkalies react with azobisformamide to produce the alkali salts of azodicarboxylic acid which may be precipitated with an excess of the base (eq. 8). On heating, the solution of the alkali azodicarboxylate decomposes with the liberation of carbon dioxide and nitrogen (eq. 9).

$$NH_2CO-N=N-CONH_2 + 2\,NaOH \rightarrow NaOCO-N=N-COONa + 2\,NH_3 \qquad (8)$$

$$2\,NaOCO-N=N-COONa + 2\,H_2O \rightarrow N_2H_4 + Na_2CO_3 + 2\,CO_2 + N_2 \qquad (9)$$

Hot concentrated hydrochloric acid decomposes azobisformamide with the evolution of carbon dioxide and nitrogen to yield biurea and ammonium chloride (127). Diels and Paquin reported (128) the formation of hydrazine when azobisformamide is treated with warm, dilute sulfuric acid. As a weak oxidizing agent, azobisformamide may react with many phenols and secondary amines used as stabilizers for polymers to produce color-forming bodies of the quinoid and diazo types.

Although the decomposition point of azobisformamide in air is high, the blowing agent can be activated by many additives which are usually employed as compounding ingredients for polymers—eg, protective agents or cure activators. These adjuncts lower the decomposition temperature and increase the decomposition rate of azobisformamide in polymers. Among the additives, certain vinyl stabilizers containing basic salts of lead, cadmium, or zinc are the most efficient activators (Fig. 4). Poly-(vinyl chloride) stabilizers containing the same cation show increased activation with the increase in stabilizer solubility (129). The activating effect of the basic metal salts has been explained (130) by the instability of azodicarboxylates believed to be first formed during the reaction of azobisformamide with the cations of these vinyl stabilizers in alkaline medium. The lead, cadmium, and zinc azodicarboxylates decompose at low temperatures and initiate the decomposition of the diamide. When barium stabilizers are present, no activation takes place, since barium azodicarboxylate is more stable thermally than the diamide.

Another group of additives that accelerate the decomposition of azobisformamide are polyols, eg, glycols and glycerol (131). Also, urea, alcoholamines, and certain organic acids (eg, oxalic and *p*-toluenesulfonic acids) lower the decomposition temperature of azobisformamide due to their hydrolytic effect on the blowing agent.
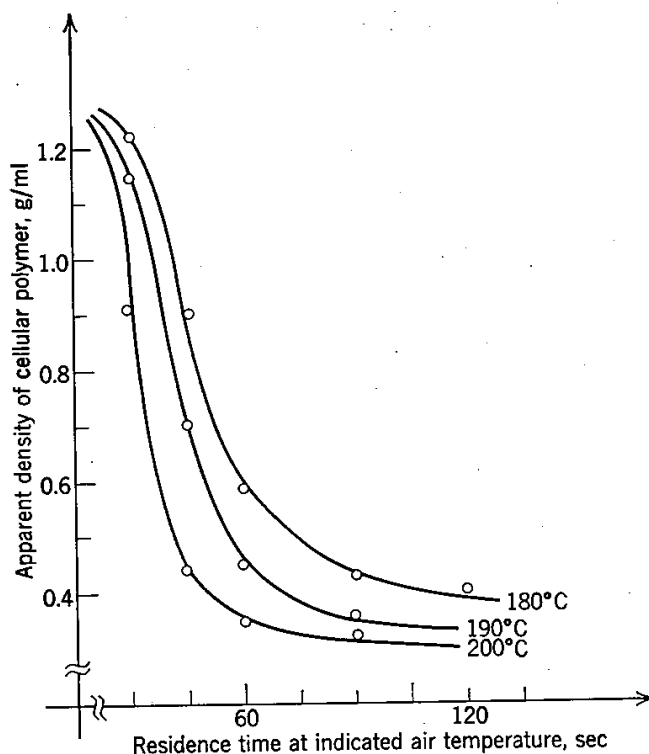
Fig. 4. Decomposition rate of 1,1'-azobisformamide in poly(vinyl chloride) stabilized with dibasic lead phthalate.

In addition to dibasic acids, dinitrosopentamethylenetetramine has been claimed (132) as an effective activator for azobisformamide. Biurea, proposed as a decomposition promoter (133) in 1957, does not decrease the decomposition temperature significantly.

The degree of activation that can be attained with vinyl stabilizers depends upon the particle size of the azobisformamide. Since the activation occurs in a heterogeneous system, the surface area of the reagents has a direct bearing on the decomposition rate. Azobisformamide of small particle size is activated more readily than azobisformamide composed of large particles (32).

Azobisformamide of very fine particle size has been observed to possess a cure-activating effect, probably due to the formation of a small quantity of free radicals during the decomposition. Aliphatic diazo compounds such as R—N=N—CO—NH(CH₂)ₙNH—CO—N=N—R, a diazodicarbonamide, and R—N=N—COO—(CH₂)ₙOCO—N=N—R, a diazodicarbonate, are known to combine blowing efficiency with crosslinking properties (134). For example, diazodicarboxylates have been reported to crosslink natural rubber quantitatively (135).

Azobisformamide and its decomposition residue are considered nontoxic and nonirritating. The actual oral toxicity (LD₅₀) of azobisformamide, as measured in Wistar rats, is greater than 6400 mg/kg body weight. The compound has recently been suggested as a bleaching and maturing agent for flour (136), and it has been accepted for this purpose by the Food and Drug Administration to a maximum level of 45 ppm (137).

Azobisformamide produces odorless, nonstaining, nondiscoloring cellular polymers. This blowing agent has been successfully used in the expansion of synthetic

and natural rubber (138), poly(vinyl chloride) compounds (139), and polyolefin resins (140). It has also been found useful in the manufacture of cellular acrylonitrile–butadiene–styrene plastics and high-impact polystyrene sheeting. The 1963 price range of azobisformamide blowing agents was $1.60–1.65/lb.

N-Substituted homologs of azobisformamide are also blowing agents for polymers, but they are less efficient than the parent compound and decompose at lower temperatures; for instance, N,N'-di-*tert*-butylazobisformamide decomposes at 170°C, N,N'-di-*n*-decylazobisformamide at 145°C, and N,N'-diphenylazobisformamide at 177°C. These compounds can be obtained from monosubstituted ureas by methods analogous to those used for making azobisformamide.

Esters of azodicarboxylic acid (azobisformic acid) (14) are conveniently prepared from hydrazine and chloroformates through the corresponding hydrazo compounds, oxidation of which yields the azodicarboxylates (134). Generally, these esters are liquids with a wide range of decomposition points (141). The diethyl ester has a decomposition point of 105–110°C and yields 129 ml nitrogen (STP)/g. It was available in Germany in 1943–1945 as Porofor 476 (I. G. Farbenindustrie) for making cellular rubber.

Salts of azodicarboxylic acid have recently been claimed as blowing agents for special applications. In slightly acidic media, the alkali salts hydrolyze readily at room temperature (142). When these salts are used in polymers which generate traces of water during crosslinking, eg, in peroxide cured polysulfide polymers, a cellular product can be obtained (143). The barium salt is useful as a blowing agent for high-melting polymers (144), eg, polypropylene, rigid poly(vinyl chloride), or ABS resin. The dry salt (available as Expandex 177 in the form of a dispersion, by National Polychemicals) decomposes at 245°C with evolution of nitrogen and carbon monoxide (eq. 10). The total gas yield is 177 ml (STP)/g.

$$\begin{array}{c} N-COO \\ \| \qquad\ \ \ Ba \\ N-COO \end{array} \longrightarrow\ BaCO_3\ +\ CO\ +\ N_2 \qquad\qquad (10)$$
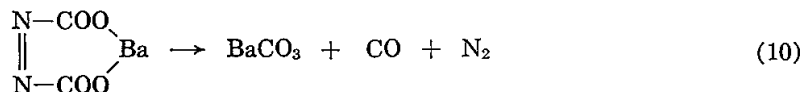
Barium azodicarboxylate hydrolyzes in presence of water and must be protected against moisture absorption to retain its efficiency. The alkali and alkaline earth azodicarboxylates are light yellow powders; they can easily be prepared from azobisformamide and the corresponding base (145).

Other aliphatic azo compounds suggested as blowing agents include sodium and potassium diazomethionates (146), and azoacetic acid esters (147).

Hydrazine

Hydrazine Salts. Hydrazine derivatives have long been recognized as potentially useful sources of nitrogen.

Phenylhydrazine was proposed as a blowing agent for rubber as early as 1920 (148). It decomposes upon heating with evolution of nitrogen and ammonia in equal volumes; the total gas yield is 207 ml (STP)/g. More recently, hydrazine and its salts, particularly oxalate and stearate (149), have been claimed as unusually effective blowing agents. Also, inorganic salts of hydrazine, eg, the mononitrate activated with ferrous sulfate or molybdenum trioxide (150), have been recommended for making cellular polymeric compositions. None of these materials has been developed commercially, however.

Hydrazones. When reacted with hydrazine, many aromatic aldehydes and ketones form crystalline, high-melting compounds known as hydrazones (151), some of which have acquired practical significance as blowing agents.

Benzil monohydrazone (C_6H_5—C(:N—NH_2)—CO—C_6H_5) (Porogène 47, Société St. Gobain, Paris; now withdrawn), a light yellow crystalline solid with a melting point of 150°C, yields nitrogen (100 ml (STP)/g) and leaves benzyl phenyl ketone as a nontoxic, yellow residue. Prior to the introduction of azobisformamide, benzil hydrazone was the only suitable blowing agent for calendered poly(vinyl chloride) sponge (152). Its relatively high decomposition temperature permitted the direct addition of the blowing agent to plasticized poly(vinyl chloride) compounds without the danger of decomposition of the blowing agent during the calendering operation.

Salicylaldehyde hydrazone, which has a decomposition point of 210–220°C and a gas yield of 90 ml nitrogen (STP)/g, is another interesting blowing agent of this class.

Hydrazides. Many of the commercially used blowing agents fall within this category.

Hydrazides of organic sulfonic acids constitute one of the most versatile and useful classes of organic blowing agents. Although derivatives of both aliphatic (153,154) and aromatic (153) sulfonic acids have been claimed in patents, only the latter are commercially important. The pure compounds of this class are mostly crystalline, nontoxic, odorless solids which can readily be obtained by reacting hydrazine with aliphatic or aromatic sulfonyl chlorides (155). Depending upon the sulfonic acid used, blowing agents with decomposition points ranging from 80 (diethylaminosulfonyl hydrazide) to 245°C (bisbenzenesulfonyl hydrazide) can be prepared. One or both —NH_2 groups of the hydrazine molecule can be substituted with alkyl and/or aryl radicals and this further adds to the diversity of useful compounds. All sulfonyl hydrazides decompose on heating with a quantitative evolution of nitrogen. This decomposition may be accelerated, or even brought to completion at room temperature, by hydroxyl-bearing solvents—eg, aliphatic alcohols or water—particularly if small quantities of alkaline substances or oxidizing agents (ferric salts, iodine, hydrogen peroxide) are also present (156). Besides nitrogen, water vapor is also generated during the decomposition; the residue consists of alkyl or aryl disulfides and thiosulfoxides. The decomposition reaction of sulfonyl hydrazides involves an internal reduction–oxidation of the sulfonyl hydrazide group (155,156).

$$4\ R—SO_2NH—NH_2 \rightarrow 4\ N_2 + 6\ H_2O + R—S—S—R + R—S—SO_2—R$$
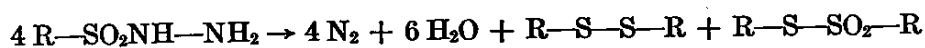
The decomposition exotherm is moderate since the reduction of the sulfonyl group proceeds endothermally and partially compensates for the exotherm generated during the oxidation of the hydrazine group. The decomposition residue is nontoxic and, in general, colorless; it does not influence the rate of crosslinking or fusion of polymers. In most instances they show adequate compatibility with polymers, and do not bloom to the surface of expanded products.

As amphoteric compounds, the sulfonyl hydrazides form crystalline salts with both acids, eg, RSO_2NHNH_2·HCl, or alkalies, eg, $RSO_2N(Na)NH_2$.

Sulfonyl hydrazides are flammable solids which ignite from a spark or flame. When ignited, they decompose rapidly in air, with or without a flame, leaving a voluminous residue. Under normal storage conditions, the compounds of this class are stable for a prolonged period of time.

Cellular polymers produced with sulfonyl hydrazides display a fine and uniform pore structure and are nontoxic and nonstaining. In most cases, the cellular products are nondiscoloring and odorless.

Since 1952, several sulfonyl hydrazides have been marketed as blowing agents for elastomers and plastics. Sulfonyl hydrazides with an asymmetric molecular configuration have been found useful only in elastomeric applications, since in many other polymers, eg, poly(vinyl chloride), they develop a mercaptan-like odor. The symmetrical hydrazides have been employed for all types of polymers.

Of the asymmetric sulfonyl hydrazides, *benzenesulfonyl hydrazide* (BSH) is the most important product commercially. The pure material (sp gr 1.43) decomposes at 104°C, and the commercially available product (Genitron BSH, Whiffen & Sons; Porofor BSH, Farbenfabriken Bayer) generates gas at about 100°C in air and at 90°C in rubber compositions. This blowing agent yields 115–130 ml nitrogen (STP)/g in addition to 195 ml steam. To improve the dispersibility of benzenesulfonyl hydrazide in elastomers, dispersions of the blowing agent in processing oils are being offered commercially. Benzenesulfonyl hydrazide is being extensively used in the production of atmospherically and pressure-blown soft rubber goods. The low decomposition temperature of the blowing agent requires careful control of processing (mixing, calendering, etc) temperatures to prevent a loss of blowing efficiency. This limits the use of benzenesulfonyl hydrazide to soft, highly plasticized stocks which do not generate heat during mixing.
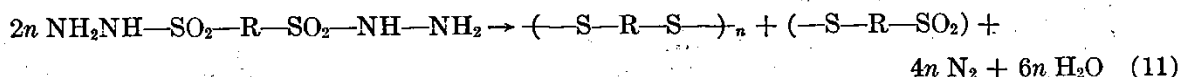
For the expansion of highly loaded rubber compounds such as are usually encountered in the manufacture of microcellular shoe soling, *1,3-benzenedisulfonyl dihydrazide* (B-13) has been recommended. The pure product melts with decomposition at 163°C; the commercially available blowing agent (Porofor B-13, Farbenfabriken Bayer) decomposes in air at 145°C and in rubber at 125°C. It liberates 170 ml nitrogen (STP)/g, the highest volume of gas among the commercial hydrazide blowing agents. Due to its higher decomposition temperature, 1,3-benzenedisulfonyl dihydrazide can be processed more safely than benzenesulfonyl hydrazide. The blowing agent is marketed in the form of a 50% paste in chloroparaffin.

Methyl carbanilate substituted with the sulfonyl hydrazide group in the para position (2), also known as *phenyl methylurethan-p-sulfonyl hydrazide*, has been reported (157) to be used in the manufacture of microcellular rubber in the U.S.S.R. It decomposes in a temperature range of 140–160°C and liberates 95–100 ml (STP)/g (158).

$$H_3COCONH \langle \bigcirc \rangle SO_2NHNH_2$$

(2)
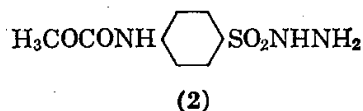
Among the symmetric hydrazides, *4,4'-oxybis(benzenesulfonyl hydrazide)* (OBSH) (159) is the most widely used compound. It is a white, crystalline solid melting with decomposition at 164°C. The commercial product (Celogen, Naugatuck Chemical Division, U.S. Rubber Co.) is sold as finely ground, oil-treated powder (sp gr 1.52), which decomposes slowly at 130°C. The most rapid and efficient gas evolution occurs at 150–160°C. When heated in dioctyl phthalates, the material generates 125 ml (STP) of noncondensable gas per gram, over 98% of which is nitrogen. In common with other difunctional sulfonyl hydrazides, 4,4'-oxybis(benzenesulfonyl hydrazide) leaves a polymeric residue which is free of volatile, odoriferous mercap-

tides. The decomposition of the difunctional derivatives can be expressed by equation 11.

$$2n \text{ NH}_2\text{NH}-\text{SO}_2-\text{R}-\text{SO}_2-\text{NH}-\text{NH}_2 \rightarrow (-\text{S}-\text{R}-\text{S}-)_n + (-\text{S}-\text{R}-\text{SO}_2) +$$

$$4n \text{ N}_2 + 6n \text{ H}_2\text{O} \quad (11)$$

4,4'-Oxybis(benzenesulfonyl hydrazide) is useful as a blowing agent for all types of elastomers and plastics. Among the latter, branched polyethylene, poly(vinyl chloride) plastisols, and epoxy and phenolic resins are currently expanded on a commercial scale with this blowing agent. It is most widely used, however, in the manufacture of thermal-insulation materials based on blends of synthetic rubbers and thermoplastics—eg, nitrile–butadiene rubber–poly(vinyl chloride). In this application, 4,4'-oxybis(benzenesulfonyl hydrazide) acts as both blowing and crosslinking agent in the absence of conventional curing agents (160). Other difunctional sulfonyl hydrazides possess similar crosslinking ability in varying degrees, depending upon the aryl or alkyl radical. 4,4'-Oxybis(benzenesulfonyl hydrazide) commanded a 1964 market price of $1.95/lb.

3,3'-Sulfonylbis(benzenesulfonyl hydrazide) (D-33) is another difunctional hydrazide that has been available commercially (Porofor D-33, Farbenfabriken Bayer). It decomposes at 148°C and gives off 110 ml nitrogen (STP)/g. The product has been primarily recommended for blowing poly(vinyl chloride) plastisol compositions (161).

Disulfonyl dihydrazide of undisclosed chemical composition (Porofor S-44, Farbenfabriken Bayer), with a gas yield of 120 ml nitrogen (STP)/g and a decomposition range of 175–180°C, has been offered for expanding polyethylene and calendered poly(vinyl chloride) compounds.

Analogs of 4,4'-oxybis(benzenesulfonyl hydrazide) derived from diphenyl sulfide (162) and diphenyl methane (163) have been patented but not yet marketed.

Trihydrazino-sym-triazene (THT) (3), also called cyanuric trihydrazide, has been suggested as a blowing agent for making cellular products based on high-melting polymers (164), eg, ABS resins, polypropylene, and rigid poly(vinyl chloride) compounds. It can be obtained by reacting cyanuric chloride or melamine with hydrazine. It decomposes at 230°C with the evolution of equal volumes of nitrogen and ammonia, and leaves melamine as residue. The theoretical gas yield is 262 ml (STP)/g; the actual gas evolution reaches 94% of the theoretical. It has been test marketed in Great Britain as Genitron THT (Whiffen & Sons).

NHNH₂
|
C
N⫻ ⫤N
| ‖
H₂NHN—C   C—NHNH₂
  ⫲N⫽

(3)
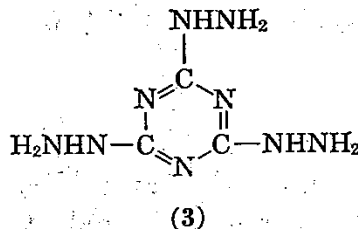
Semicarbazides

Sulfonyl Semicarbazides. Sulfonyl semicarbazides of the general formula R—SO₂—NH—NH—CO—NH₂ constitute a distinctly new class of organic blowing agents (165). The individual members of this group can be synthesized by reacting the corresponding sulfonyl hydrazides with an alkali cyanate in an acidic medium.

The semicarbazides are soluble in alkalies, from which they can be precipitated in a pure form by acidification.
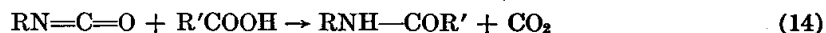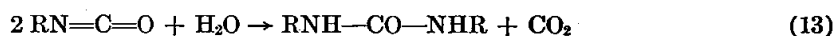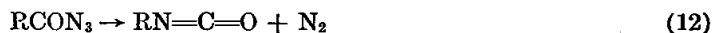
The semicarbazides exhibit greater heat stability than the hydrazides from which they are derived. The conversion to semicarbazides raises the melting and the decomposition point, and increases the gas yield. Liquid hydrazides, eg, methanesulfonyl hydrazide (dec 70°C), are transformed into crystalline, stable semicarbazides, eg, methanesulfonyl semicarbazide (dec 194°C). The decomposition of the blowing agents of this group leads to the evolution of nitrogen and carbon dioxide in quantities at least 30% higher than one mole of gas for each sulfonyl semicarbazide group in the molecule.

Typically, the semicarbazides are high-temperature blowing agents, useful in the preparation of cellular polymers based on high-melting polymers. One compound of this class, 4,4'-oxybis(benzenesulfonyl semicarbazide), has been test marketed in the United States as Celogen BH (Naugatuck Chemical Division, U.S. Rubber Co.). The compound decomposes in air at 213°C and liberates 145 ml gas (STP)/g. The evolved gas is composed of nitrogen (65%), carbon dioxide (33%), and carbon monoxide (2%). This blowing agent has been recommended for the expansion of linear polyethylene, polypropylene, and ABS resins.

Azides

Blowing agents of the azide type are derivatives of either carboxylic or sulfonic acids. They can be prepared by treating the corresponding acid hydrazides with nitrous acid or by reacting the acid chlorides with alkali azides. The blowing agents of this group are white, crystalline products which give off nitrogen upon heating. The thermal decomposition of azides is accompanied by a high exotherm. The residue of the decomposition is nonstaining and usually white. The azide blowing agents are flammable and shock-sensitive solids. They should be handled carefully to avoid spontaneous and rapid decomposition.

Carbonyl Azides. Organic *carbonyl azides* (166), particularly those derived from aromatic acids, eg, benzoyl azide, *p-tert*-butylbenzoyl azide, are soluble in ester plasticizers. This facilitates their incorporation into such thermoplastic resins as poly-(vinyl chloride) homo- and copolymers. They also disperse easily in all types of elastomers and millable plastics. Upon heating, carbonyl azides yield nitrogen and an isocyanate (eq. 12). The latter can be used as an additional source of gas when reacted with water (eq. 13) or acid (eq. 14). If the decomposition takes place in the presence of compounds containing hydroxyl or amine groups, residual diisocyanate may act as a crosslinking agent.

$$\text{RCON}_3 \rightarrow \text{RN=C=O} + \text{N}_2 \tag{12}$$

$$2 \text{ RN=C=O} + \text{H}_2\text{O} \rightarrow \text{RNH—CO—NHR} + \text{CO}_2 \tag{13}$$

$$\text{RN=C=O} + \text{R'COOH} \rightarrow \text{RNH—COR'} + \text{CO}_2 \tag{14}$$

The *p-tert*-butylbenzoyl azide (167) with a melting point of 64°C and a gas yield of 110 ml nitrogen (STP)/g has been test marketed. Other carbonyl azides which have been suggested as blowing agents for polymers include benzazide (166), terephthalazide (168), and *p*-carbomethoxybenzazide (169).

Sulfonyl Azides. Among the *sulfonyl azides* which have been claimed as blowing agents (170,171), diphenyl-4,4'-disulfonyl diazide (172) has been of some value as a blowing and crosslinking agent for thermoplastic resins. The product is a white

solid decomposing at 144–145°C. During the thermal decomposition, in addition to nitrogen (122 ml (STP/g), free radicals are formed which are capable of producing solvent-resistant, crosslinked polymers. Crosslinked cellular polystyrene (173), polyethylene (174), and alkyd resins (175) have been successfully prepared by the use of diphenyl-4,4'-disulfonyl diazide. The blowing agent was test marketed in the United States in 1958–1960 as Nitropore (National Polychemicals). It failed to gain acceptance because the high decomposition exotherm led to partial degradation of the cellular polymers and has been withdrawn by the manufacturer.

N-Substituted 5-amino-1,2,3,4-thiatriazoles have been claimed as blowing agents for elastomers and plastics (176). The N-disubstituted derivatives of the general formula (4) can be obtained by nitrosation of the corresponding thiosemicarbazides

$$RR'N-C\underset{S}{\overset{\displaystyle N-N}{\bigvee}}N$$
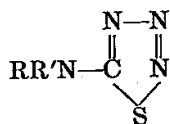
(4)

(177). Depending upon the substituents, blowing agents with decomposition points from as low as 51° (the dimethyl derivative) to as high as 162°C (the piperazine derivative) can be obtained. Unlike azides, the thiatriazoles give off their nitrogen at a controllable rate. Simultaneously with the evolution of nitrogen, sulfur is also split off during the thermal decomposition. The liberation of sulfur is claimed to be advantageous in applications involving elastomers which are susceptible to sulfur vulcanization. One compound of this class, Porofor TR (Farbenfabriken Bayer), a morpholine derivative, has been used in Germany in the production of cellular poly(vinyl chloride) compositions based on plastisols. The blowing agent decomposes at 112°C and yields 130 ml nitrogen (STP)/g. Because of the presence of a minor quantity of sulfur among the decomposition products, the blowing agent should be compounded with stabilizers resistant to sulfur staining when light-colored cellular vinyl plastics are to be produced. One of the disadvantages of this material is the fact that cellular products made with it may cause skin irritation. The unsubstituted 5-amino-thiatriazole, although claimed as a useful blowing agent for plastics (178), has not been offered commercially.

N-Nitroso Compounds

The N-nitroso derivatives of secondary amines and N-substituted amides form an important class of blowing agents which includes two commercial products—dinitrosopentamethylenetetramine and N,N'-dimethyl-N,N'-dinitrosoterephthalamide.

N-Dinitrosoamines. Dinitrosopentamethylenetetramine (DNPT) (5) can be

$$\begin{array}{c} H_2C-N-CH_2 \\ |\quad|\quad| \\ ON-N\ HCH\ N-NO \\ |\quad|\quad| \\ H_2C-N-CH_2 \end{array}$$
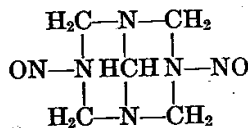
(5)

obtained by the nitrosation of an ammonia–formaldehyde solution (molar ratio $NH_3:CH_2O = 2:3$) with sodium nitrite in the presence of acetic acid (179). The method of nitrosation involving the addition of an acid to a cold mixed solution of hexamethylenetetramine and sodium nitrite is more convenient. In this in-

stance, either organic acid (eg, acetic acid (180)) or mineral acids (eg, hydrochloric (181), nitric (179), or sulfuric (182) acids) may be used. Yields of between 75 and 79% based on hexamethylenetetramine have been reported. An excess of nitrous acid leads to the formation of trimethylenetrinitrosoamine (mp 105°C), an undesirable by-product. Because of the instability of dinitrosopentamethylenetetramine in acidic medium, the nitrosation should be carried out with only the theoretical quantity of acid. Better yields and a more stable product have been claimed to be obtained by neutralizing any excess of acid with alkaline materials (183).

After recrystallization from hot alcohol, dinitrosopentamethylenetetramine forms light yellow needles which melt with decomposition at 207°C. Commercial grades have a lower decomposition point, usually between 190 and 200°C. The compound has a limited solubility in pyridine, morpholine, and ethyl acetoacetate, and is readily soluble in dimethylformamide and dimethyl sulfoxide. It is virtually insoluble in water, alcohols, aliphatic and aromatic hydrocarbons, and most esters.

Dinitrosopentamethylenetetramine is particularly sensitive to mineral acids and certain salts of these acids (eg, zinc chloride), which may cause a violent decomposition of the blowing agent at low temperatures and result in ignition of the mixture. In dilute hydrochloric acid, hydrolysis occurs at temperatures around 100°C (179).

$$C_5H_{10}(NO)_2N_4 + 3\,H_2O \rightarrow 5\,CH_2O + 2\,N_2 + 2\,NH_3$$
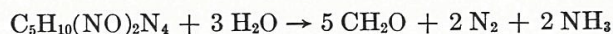
The effect of acids on the decomposition temperature of dinitrosopentamethylenetetramine is proportional to their dissociation constants; the higher the dissociation constant, the lower the temperature (184), as shown in Table 2.

Table 2. Effect of Acids on Decomposition Temperature of Dinitrosopenta-methylenetetramine

Acid	pK$_a$ at 25°C	Decomp temp, °C
hydrochloric acid, conc	<1.0	room temp with ignition
oxalic acid		60–70
K_1	1.19	
K_2	4.21	
salicylic acid		100
K_1	2.97	
K_2	13.44	
phthalic acid		
K_1	2.89	
phthalic anhydride	5.41	115
benzoic acid	4.20	130
boric acid	9.24	130
fatty acids	>10	180

Dinitrosopentamethylenetetramine is more stable in the presence of cold alkalies, but at elevated temperatures it decomposes readily in an alkaline medium. Organic bases such as urea, biuret–water, and polyhydric alcohols also lower the decomposition temperature. In an inert medium, a sustained thermal decomposition occurs above 180°C producing essentially nitrogen and a solid white residue. Among the gaseous decomposition products, minor quantities of nitrous oxide, carbon dioxide, oxygen, water, and formaldehyde have been identified. In acidic medium, trace amounts of

amines are believed to be evolved. The solid residue formed upon decomposition has not been identified. The decomposition reaction is highly exothermic.

The compound is an oxidizing agent and can be reduced quantitatively with titanous chloride in an acidic medium. Reducing compounding ingredients (eg, thiophenols or mercaptides) should not be brought in direct contact with it in order to avoid violent reaction at processing temperatures. It is a flammable solid, easily ignited by a free flame. In the dry state, it is sensitive to impact and friction, but can be detonated only with considerable difficulty.

The utility of dinitrosopentamethylenetetramine as an efficient, nonstaining, nondiscoloring blowing agent was discovered by Briggs and Scharff (15). It is commercially available in the form of blends consisting of the dinitrosoamine with inorganic diluents, processing aids, and/or stabilizers. In the United States, products containing 42% dinitrosopentamethylenetetramine (Opex 40, National Polychemicals; Unicel ND, Du Pont) are most commonly used, but 80% active compounds (Opex 80, National Polychemicals; Unicel NDX, Du Pont; Vulcacel BN, Arnold and Hoffman Co., Providence, R.I.) are also available. The latter products are more popular in Europe. The diluent facilitates handling and lessens the fire hazard associated with the use of the active ingredient. Ground nonreinforcing silica or washed neutral clays are usually employed as inorganic diluents. Dinitrosopentamethylenetetramine is insoluble in elastomers and plastics, but disperses readily, particularly if treated with processing oils or plasticizers which are compatible with the polymer. The dispersibility of dinitrosopentamethylenetetramine may be further enhanced by coating the blowing agent particles with selected surfactants (185). To stabilize it when it is in contact with strong acids, the addition of salts of weak organic acids and fatty acid esters of alkylhydroxylamines has been suggested (186). Similar effects are obtained when an oxide, hydroxide, or carbonate of calcium, barium, zinc, or magnesium is used as a stabilizer (187).

The commercial 42% blend of dinitrosopentamethylenetetramine is a cream-colored, odorless, nonhygroscopic solid in powder form (sp gr 1.91). Upon decomposition, the product liberates approximately 105 ml noncondensable gases (STP)/g. Under normal conditions, the storage stability of the commercial composition is excellent. The product has a very low level of acute toxicity, and is only a minor skin irritant.

The processing stability of dinitrosopentamethylenetetramine blowing agents is good, particularly in neutral or basic media. The thermal decomposition is independent of pressure, hence the blowing agent can be used for the manufacture of pressure-expanded polymers. In the absence of activator, dinitrosopentamethylenetetramine blowing agents liberate gases at temperatures higher than those of conventional vulcanization or fusing. In practice, to lower the decomposition temperature of the blowing agent, numerous additives have been used advantageously. Organic acids, eg, salicylic or phthalic acids, substantially decrease the decomposition temperature and permit the development of vulcanizates with very fine cells. However, the end-products display a disagreeable "fishy" odor. Another disadvantage of acidic promoters is their cure-retarding effect on rubber compounds. Organic sulfonic acids have been suggested as additives for the production of low-density sponge (188).

More important than the acidic additives are basic promoters for dinitrosopentamethylenetetramine. They decrease the decomposition temperature to a lesser degree than most acidic materials, but still bring it into a practical temperature range for a

rapid gas generation. Of the basic materials, urea and urea-containing mixtures and complexes have gained practical importance in controlling the decomposition of dinitrosopentamethylenetetramine (82,189). Cellular vulcanizates prepared with this compound in the presence of urea have a characteristic, faintly ammoniacal odor. This odor is fugitive and can be dissipated by a heat treatment (annealing) of cellular products. Urea in conjunction with *C*-cetyl betaine (Aquarex NS, registered trademark of E. I. du Pont de Nemours & Co., Inc.) or melamine with diethylene glycol (190) have also been recommended for odor control.

Neutral promoters also play an important role in the activation and odor control of dinitrosopentamethylenetetramine-blown sponge. The most commonly used additives of this class are glycols (diethylene, triethylene, polyethylene glycols). In addition to the promoters, deodorants are employed to counteract the readily discernible odor of vulcanizates expanded with dinitrosopentamethylenetetramine.

The basic and neutral promoters exert a pronounced activating effect on the vulcanization of rubber. This effect, combined with a mild cure activation of dinitrosopentamethylenetetramine, particularly at higher concentrations, makes possible the development of fast-curing compounds with low levels of conventional accelerators.

Dinitrosopentamethylenetetramine, which was introduced in 1947 (191), is the most widely used blowing agent in the rubber industry, but has gained only limited acceptance in plastics. Cellular rubber goods based on natural and synthetic elastomers are being manufactured with dinitrosopentamethylenetetramine for a broad line of products such as microcellular shoe soling, automotive weatherstripping, thermal insulation, and children's balls. Dinitrosopentamethylenetetramine has been suggested for use in poly(vinyl chloride), but due to its high decomposition exotherm and its sensitivity to traces of hydrochloric acid, the resulting cellular products are discolored, sometimes degraded, and display an unpleasant odor. Better results have been claimed to be obtainable with poly(vinyl chloride) compounds containing boric acid and urea as promoters (192). The low unit price, currently 62¢/lb for the 42% blend, and the high gas yield combine to make this compound the most economical nitrogen-releasing blowing agent.

N,N'-Dinitrosoamides. In this group, *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide has received the greatest commercial use.

The *N-methyl-N-nitrosoamides* of aliphatic acids have been cited in the patent literature (15,193,194) as low-temperature blowing agents; however, these compounds have not been commercially developed because of their poor storage stability. A more stable analog is that derived from terephthalic acid.

N,N'-Dimethyl-N,N'-dinitrosoterephthalamide (NTA) (195) can be prepared by nitrosation of *N,N'*-dimethylterephthalamide in nitric acid solution (196). The product is an odorless, yellow crystalline solid melting with decomposition at 118°C. It liberates 180 ml nitrogen (STP)/g, with traces of water and carbon dioxide. The residue of the decomposition is dimethyl terephthalate, a white crystalline solid (mp 140°C). It has limited compatibility with most polymers, resulting in the formation of a white bloom on the surface of cellular polymers expanded with more than 5% of the blowing agent. In the pure state, the compound evolves no gas during extended (140 hr) storage at 60°C. It can be kept indefinitely without significant decomposition at ambient temperatures (max 40°C). The thermal stability is reduced by mixing the blowing agent with numerous other materials. Alkalies de-
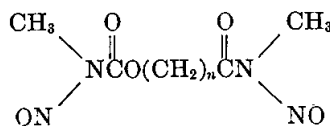
crease its stability in direct proportion to their alkalinity and solvating power. In the presence of strong alkalies, eg, alcoholic solutions of sodium hydroxide, diazomethane may be formed. Strong amines, eg, ethylenediamine, cause instantaneous decomposition. Dissolved in polar solvents (eg, isopropanol or ethylene glycol), N,N'-dimethyl-N,N'-dinitrosoterephthalamide decomposes completely at room temperature within a few hours. The effect of mineral acids, which in general promote hydrolysis of the compound, is less pronounced. Many other materials normally considered inert (eg, poly(vinyl chloride) resins or ester plasticizers), significantly decrease the decomposition temperature and bring about a slow liberation of nitrogen under ambient conditions. The blowing agent can be made less sensitive to these compounding ingredients by coating it with a modifier, eg, glycolic esters of fatty acids (197). Exposure to sunlight and other sources of ultraviolet radiation result in a color change from yellow to green. This color change has no effect on the performance or thermal stability of the blowing agent.

N,N'-Dimethyl-N,N'-dinitrosoterephthalamide is a weak deflagrating explosive and ignites easily from spark or flame; its burning rate is extremely fast. It has a very low level of acute toxicity and is a minor skin irritant.

Commercially, this compound is available in the form of a blend (containing 70% of active ingredient) with mineral oil as the diluent. The commercial product (Nitrosan, Du Pont) is an odorless, yellow-colored, nonhygroscopic crystalline powder (sp gr 1.20) which melts with decomposition at 105°C. Prolonged heating at a lower temperature, eg, 80–90°C, will result in a sustained and rapid decomposition. The gas yield of the blend is 126 ml (STP)/g.

N,N'-Dimethyl-N,N'-dinitrosoterephthalamide is an efficient, nondiscoloring, nonstaining blowing agent suitable for the expansion of polymers that can be blended with it below 70°C. The material has found its widest application in poly(vinyl chloride), compositions (198). Because of its low decomposition exotherm this blowing agent can be used in the preparation of thick sections of cellular vinyl compositions without the danger of polymer degradation. The most efficient utilization of this blowing agent is achieved by the activation with mild alkaline materials, eg, calcium sulfonates of paraffinic oils. It has been employed as a blowing agent for castable polyurethan elastomers and silicone rubbers and has also been suggested for the expansion of liquid polyamide and epoxy resins. In 1963 the 70% blend was priced at $2.00–2.25/lb.

Other Dinitroso Compounds. Closely related to the N-nitrosoamides already described are N-substituted nitrosourethans and ureas (193). The blowing agents of this class liberate a high volume of gas (2 moles for each —N(NO)CO— group) consisting of equal parts of nitrogen and carbon dioxide. Among the most efficient blowing agents of this group are N,N'-dimethyl-N,N'-dinitrosodimethylenediurethan (dec 133°C), N,N'-dimethyl-N,N'-dinitrosotetramethylenediurethan (dec 125°C, mp 123°C), both (6), where n = 2 or 4, respectively, and N,N'-dinitrosoethyleneurea (199).

$$\text{CH}_3 \diagdown \underset{\text{ON} \diagup}{\text{N}}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{O}(\text{CH}_2)_n\overset{\overset{\text{O}}{\|}}{\text{C}}\underset{\diagdown \text{NO}}{\text{N}}\diagup \text{CH}_3$$

(6)

The *N*-nitrosoamides of sulfonic acids (eg, *p*-cresoldisulfonic acid (200), ethyl-enebis(benzenesulfonic acid), and *p,p'*-oxybis(benzenesulfonic acid) (201) are known as gas-generating chemicals, but have not been used commercially.

An interesting group of liquid blowing agents are the *N*-nitroso-β-aminoketones, eg, *N*-ethyl-*N*-nitrosodiacetoneamine (derived from mesityl oxide and ethylamine), and *N*-nitrosotriacetoneamine (derived from phorone and ammonia). The *N*-nitroso-β-aminoketones decompose when heated with either alkali (202) or acids (203) with the evolution of nitrogen. The *N*-nitrosotriacetoneamine was test marketed in the United States in 1955–1956. In addition to the mononitroso compounds, *N*-dinitroso-β-aminoketones (204) have been considered as blowing agents for polymers.

Since blowing agents are used exclusively in the preparation of expanded elastomers and plastics, their future is tied to new developments in cellular polymers. In the last decade, 1953–1963, the production of cellular polymers has continued to grow, in some instances even faster than the output of base polymers. The wide acceptance of cellular polymers in industrial and consumer applications presages an increasing consumption of blowing agents in the future.

Bibliography

1. C. Hancock, Brit. Pats. 11,032 (Jan. 20, 1846) and 11,575 (Feb. 10, 1847). W. Brockedon and T. Hancock, Brit. Pat. 11,455 (Nov. 19, 1846).
2. T. Forster and J. Heartfield, Brit. Pats. 2,715 (Sept. 2, 1868) and 3,215 (Oct. 20, 1868). P. B. Cow and J. Hill, Brit. Pat. 3,301 (Oct. 28, 1868).
3. *Rubber Age* (*London*) **1**, 134 (1920). *India Rubber World* **80** (5), 79 (1929).
4. *India Rubber World* **80** (7) 53 (1929); **81** (5), 88 (1930).
5. *Caoutchouc Guttaperche* **24,** 13663 (1927).
6. E. V. Osberg, *India Rubber World* **97** (2), 37 (1937). L. Cooper, *The Story of Expanded Rubber*, The Expanded Rubber Co., Ltd.
7. F. Pfleumer, Ger. Pat. 249,777 (1912; applied 1910).
8. C. L. Marshall, U.S. Pats. 1,501,791 (1924) and 1,551,110 (1925).
9. G. P. Denton (to Rubatex Products, Inc.), U.S. Pat. 1,905,269 (1930).
10. D. Roberts and T. A. Scott (to Rubatex Products, Inc.), U.S. Pat. 2,086,513 (1934). H. R. Minor (to Industrial Process Corp.), U.S. Pat. 2,157,243 (1939). F. W. Peel (to Rubatex Products), U.S. Pat. 2,158,083 (1939).
11. *Rubber World* **47**, 164 (1940).
12. D. Roberts and L. Cooper (to Rubatex Products), U.S. Pat. 2,268,621 (1942). L. Cooper and D. Roberts (to Rubatex Products), U.S. Pat. 2,283,316 (1942). C. R. Cuthbertson (to U.S. Rubber Co.), U.S. Pat. 2,291,213 (1942). H. Pfleumer (to Rubatex Products), U.S. Pat. 2,297,022 (1942).
13. M. Bogemann, R. Schroetter, and P. Stoeklin (to I. G. Farbenindustrie A.G.), Fr. Pat. 890,162 (1943; Ger. priority of June 12, 1941).
14. E. Mueller and A. Hoechtlen (to Farbenfabriken Bayer A.G.), Ger. Pat. 871,835 (1953; applied Jan. 28, 1943).
15. A. S. Briggs and G. E. Scharff (to Imperial Chemical Industries Ltd.), Brit. Pat. 587,023 (1947; applied Nov. 3, 1944).
16. N. Platzer (to Monsanto Chemical Co.), U.S. Pat. 3,072,581 (1963). F. A. Carlson and N. Platzer (to Monsanto), U.S. Pat. 3,084,126 (1963).
17. J. C. Houston and J. J. Tress (to Koppers Co., Inc.), U.S. Pat. 2,941,964 (1960). A. R. Ingram (to Koppers), U.S. Pat. 2,941,965 (1960). C. H. Pottenger (to Koppers), U.S. Pat. 3,089,857 (1963).
18. A. S. Aase and L. L. Bolstad (to Minneapolis-Honeywell Regulator Co.), U.S. Pat. 2,831,820 (1958). L. Keller, H. Reinhard, and R. Petri (to Badische Anilin- & Soda-Fabrik A.G.), Ger. Pat. 1,110,408 (1961).
19. K. Krebs and P. F. Urich (to Union Carbide Corp.), U.S. Pat. 2,845,396 (1958).
20. G. R. Sprague and F. M. Scantlebury, Jr. (to B.F. Goodrich Co.), U.S. Pat. 2,737,503 (1956).

21. F. Stastny and R. Gaeth (to Badische Anilin- & Soda-Fabrik A.G), U.S. Pat. 2,681,321 (1954). J. L. Mladinich (to Monsanto), U.S. Pat. 2,864,778 (1958). L. C. Rubens (to The Dow Chemical Co.), U.S. Pat. 2,878,194 (1959). A. A. Aykanian and F. Carlson, Jr. (to Monsanto), U.S. Pat. 2,905,972 (1959). L. C Rubens (to Dow), U.S. Pat. 2,952,594 (1960). S. P. Nemphos (to Monsanto), U.S. Pat. 2,956,960 (1960). A. A. Aykanian and F. A. Carlson, Jr. (to Monsanto), U.S. Pat. 2,945,261 (1960). G. F. D'Alelio (to Koppers), U.S. Pat. 2,983,692 (1961). P. C. Chaumeton (to Shell Oil Co.), U.S. Pat. 2,986,537 (1961). E. G. Pollard and L. C. Rubens (to Dow), U.S. Pat. 3,013,996 (1961). H. A. Wright (to Koppers), U.S. Pat. 3,060,138 (1962). E. V. Galizia (to Koppers), U.S. Pat. 3,063,954 (1962).

22. J. G. Hawkins (to Whiffen & Sons, Ltd.), Brit. Pat. 818,224 (1959).

23. C. B. Frost (to General Tire & Rubber Co), U.S. Pat. 3,072,582 (1963). R. E. Knox and J. A. Margedant, Jr. (to E. I. du Pont de Nemours & Co., Inc.), U.S. Pat. 3,079,641 (1963). R. E. Knox, *Chem. Eng. Progr.* **57** (10), 40 (1961).

24. The Dow Chemical Co., Brit. Pat. 837,723 (1960). L. C. Rubens and D. Urchick (to Dow), U.S. Pat. 2,948,664 (1960).

25. D. D. Lineberry (to Union Carbide), U.S. Pat. 3,052,643 (1962). Farbwerke Hoechst A.G., Brit. Pat. 890,398 (1962).

26. R. P. Toohy, *Chem. Eng. Progr.* **57** (10), 52 (1961). M. Wismer, G. Hydro, and W. R. Hydro (to Pittsburgh Plate Glass Co.), U.S. Pat. 3,051,665 (1962).

27. J. Lenz and H. Scheuermann (to Badische), Ger. Pat. 959,408 (1957).

28. A. Cooper, *Trans. Inst. Rubber Ind.* **18**, 51–57 (1942). F. Lober, *Angew. Chem.* **64**, 65–76 (1952). R. A. Reed, *Plastics Progr.* **1955**, 51–80 (1956). G. Hofmann and R. Mehring, *Plaste Kautschuk* **3**, 58–60 (1956). H. A. Scheurlen, *Kunststoffe* **47**, 446–454 (1957). E. Ferraris, *Materie Plastiche* **24**, 260–271 (1958). R. A. Reed, *Brit. Plastics* **33** (10), 468–472 (1960). H. R. Lasman, *Modern Plastics Encyclopedia* **40** (1A), 422–430 (1962).

29. *Trans. Inst. Rubber Ind.* **18**, 51 (1942).

30. B. A. Hunter and D. L. Schoene, *Ind. Eng. Chem.* **44**, 120 (1952). R. A. Reed, *Plastics Progr.* **1955**, 57, 62 (1956).

31. R. H. Hansen, *SPE J.* **18**, 77, 79 (1962).

32. H. R. Lasman and J. C. Blackwood, *Plastics Technol.* **9** (9), 37 (1963).

33. A. Freedlander and W. G. Goodwin (to Rubber Development Co.), U.S. Pat. 1,536,288 (1925).

34. A. F. Hardmann (to Wingfoot Corp.), U.S. Pat. 2,200,473 (1940).

35. J. H. Kelly, Jr. (to General Tire & Rubber), U.S. Pats. 2,564,401 (1947), 2,592,708 (1948), and 2,643,981 (1953).

36. W. Norris. *India Rubber World* **81** (10), 53 (1929).

37. C. Hancock, Brit. Pat. 11,032 (1846) and 11,575 (1847). British Rubber Producers Research Association, Brit. Pat. 540,917 (1941).

38. A. Hochtlen and U. Droste (to Farbenfabriken Bayer A.G.), Ger. Pat. 913,474 (1954).

39. Sorbo Ltd., Brit. Pat. 728,666 (1955).

40. L. F. Bornstein, *Forest Prod. J.* **8** (10), 51 (1956).

41. A. G. Gumbolt and E. Heitzer (to Farbwerke Hoechst A.G.), U.S. Pat. 2,913,424 (1959).

42. J. F. Taylor (to Ansul Chemical Co.), U.S. Pat. 2,602,784 (1952).

43. A. A. Baum (to Du Pont), U.S. Pat. 2,544,483 (1951).

44. R. Kern, W. N. Grohs, and F. Blumel (to Rhein-Chemie G.m.b.H.), U.S. Pat. 2,891,016 (1959).

45. A. Horney and G. McFadden (to Ohio State University, Research Foundation), U.S. Pat. 2,466,027 (1949).

46. *India Rubber World* **82** (8), 88 (1930). *Oil, Paint, Drug Reptr.* **142** (15), 44 (1942). R. E. Wood (to Van Cleef Bros.), U.S. Pat. 2,368,190 (1945). D. V. Sarbach (to Goodrich), U.S. Pat. 2,613,189 (1952).

47. J. D. Nelson and P. V. Steenstrup (to General Electric Co.), U.S. Pat. 2,446,429 (1948). R. J. Brinheman (to Koppers), U.S. Pat. 2,582,228 (1946).

48. M. Carter (to Firestone Tire & Rubber Co.), U.S. Pats. 2,290,622 (1942) and 2,381,380 (1945).

49. Imperial Chemical Industries, Brit. Pat. 524,063 (1940).

50. Du Pont, Brit. Pat. 753,259 (1956). L. E. Nye (to U.S. Rubber), U.S. Pat. 2,461,761 (1949).

51. W. T. Ten Broeck, Jr. (to Wingfoot Corp.), U.S. Pat. 2,478,879 (1949). T. W. Sarge and F. H. Justin (to Dow), U.S. Pat. 2,695,427 (1954).

52. H. L. Parry and B. O. Blackburn (to Shell Chemical Co.), U.S. Pat. 2,739,134 (1956).

53. L. Sauer and O. Reimann, Ger. Pat. 1,109,880 (1961).

54. J. McLaughlin (to Rohm & Haas Co.), U.S. Pat. 2,548,438 (1951).

55. W. J. Wayne (to Du Pont), U.S. Pat. 2,628,945 (1953).

56. E. W. Gluesenkamp (to Monsanto Chemical Co.), U.S. Pats. 2,572,568 (1951) and 2,610,157 (1952).

57. D. Roberts and L. Cooper (to Rubatex Products), U.S. Pat. 2,268,621 (1942). H. Pfleumer (to Rubatex Products), U.S. Pat. 2,297,022 (1942).

58. R. DeFries, *Trans. Inst. Rubber Ind. (London)* **6**, 476 (1930).

59. G. Cuthbertson (to U.S. Rubber), U.S. Pat. 2,360,049 (1944).

60. W. V. Smith (to U.S. Rubber), U.S. Pats. 2,285,843 (1942) and 2,351,555 (1944). E. T. Rainier and D. M. French (to U.S. Rubber), U.S. Pat. 2,371,707 (1945).

61. I. L. Newell (to United Aircraft Corp.), U.S. Pat. 2,626,968 (1953).

62. J. S. Strong (to Rohm & Haas), U.S. Pat. 2,821,513 (1958).

63. H. Z. Lecher and F. H. Adams (to American Cyanamid Co.), U.S. Pat. 2,977,329 (1961).

64. L. Talalay, J. A. Talalay, and T. F. Bush (to B.F. Goodrich), U.S. Pat. 2,758,980 (1956).

65. R. C. Wade (to Metal Hydrides, Inc.), U.S. Pat. 2,930,771 (1960).

66. T. F. Bush (to B.F. Goodrich), U.S. Pat. 2,909,493 (1959).

67. W. J. Vakousky (to B.F. Goodrich), U.S. Pat. 3,084,127 (1963).

68. R. C. Wade and P. L. Blanchard (to Metal Hydrides, Inc.), U.S. Pat. 2,951,819 (1960).

69. R. C. Wade, *Ind. Eng. Chem.* **52**, 20–21 (1960).

70. *Silicon Oxyhydride*, Bulletin F-7985, Linde Air Products Co., Div. of Union Carbide Corp., April 15, 1952. Wagner and Pines, *Ind. Eng. Chem.* **44**, 32 (1952).

71. J. A. Talalay, U.S. Pat. 2,432,353 (1947).

72. Dunlop Rubber Co., Ltd., Brit. Pat. 326,210 (1930).

73. E. J. Bethe (to U.S. Rubber), U.S. Pat. 2,567,988 (1951).

74. P. Schidrowitz and R. Ungar, Brit. Pat. 538,624 (1941).

75. G. M. Hamilton (to Callender's Cable and Construction Co., Ltd.), U.S. Pat. 2,404,171 (1952).

76. E. Mueller, H. Pfeffer, and P. Hope (to Farbenfabriken Bayer), Ger. Pat. 851,848 (1952).

77. Hubron Rubber Chemicals, Ltd., and C. E. Webb, Brit. Pat. 650,336 (1951).

78. H. D. Glenn (to U.S. Rubber), U.S. Pat. 2,634,243 (1953).

79. M. W. Harman (to Monsanto), U.S. Pat. 2,195,623 (1940; applied Sept. 1, 1937).

80. F. Becke and K. Wick (to Badische), U.S. Pat. 3,065,189 (1962).

81. R. H. Koppel, Ger. Pat. 563,165 (1931).

82. T. F. Walker and H. D. Williams (to Du Pont), U.S. Pat. 2,754,276 (1956).

83. Th. Punshon, Jr., and I. Williams (to J. M. Huber Corp.), U.S. Pat. 2,480,814 (1949).

84. G. M. O'Neal (to The Sherwin-Williams Co.), U.S. Pat. 2,668,152 (1954).

85. H. F. Schwarz (to Sherwin-Williams), U.S. Pat. 2,707,707 (1955). H. F. Schwarz, *India Rubber World* **114**, 211–212, 219 (1946).

86. L. Cooper and D. Roberts (to Rubatex Products), U.S. Pat. 2,283,316 (1942).

87. W. R. Pryer, *Rev. Gen. Caoutchouc* **27**, 721–724 (1950).

88. H. Scheurlen and K. L. Schmidt (to Farbenfabriken Bayer), Ger. Pat. 1,109,876 (1961).

89. N. I. Sax, *Dangerous Properties of Industrial Materials*, 2nd ed., Reinhold Publishing Co, New York, p. 1051.

90. T. L. Davis and K. C. Blanchard, *J. Am. Chem. Soc.* **51**, 1794 (1929).

91. R. A. Reed, *Brit. Plastics* **33** (10), 468 (1960).

92. H. Webber (to Whiffen & Sons, Ltd.), Brit. Pat. 827,996 (1960).

93. C. S. Argyle, E. Vero, H. Webber, and R. A. Reed (to Whiffen & Sons, Ltd.), Brit. Pat. 838,064 (1960).

94. K. Yokose, M. O. Watanabe, and I. Yoshida (to Sumitomo Electric Industries, Ltd.), Brit. Pat. 864,199 (1961).

95. *BIOS (British Intelligence Objectives Subcommittee) Final Report 1729*, Item 22, p. 8.

96. F. Heusler, *Ann.* **260**, 227 (1890).

97. G. A. Rubber and M. Mancinelli (to Soc. Italiana Pirelli), Ital. Pat. 395,372 (1942).

98. R. F. Sterling (to Westinghouse Electric Co.), U.S. Pat. 2,608,536 (1952).

99. E. B. McMillan and A. R. Olson (to United Shoe Machinery Corp.), U.S. Pat. 2,678,293 (1954).

100. H. H. Richmond and M. Tomiuk (to U.S. Rubber), U.S. Pat. 2,448,154 (1948).

101. H. H. Richmond (to U.S. Rubber), U.S. Pat. 2,448,155 (1948).

102. E. S. Blake (to Monsanto), U.S. Pat. 2,335,730 (1943).

103. W. B. Hardy and F. H. Adams (to American Cyanamid), U.S. Pats. 2,766,226 and 2,766,228 (1956).

104. Wm. H. von Glahn and B. Rudner (to General Aniline & Film Corp.), U.S. Pats. 2,828,298 and 2,828,300 (1958).

105. W. B. Hardy and F. H. Adams (to American Cyanamid), U.S. Pats. 2,766,227 and 2,766,229 (1956).

106. R. L. Schlessinger (to U.S. Rubber), U.S. Pat. 2,588,885 (1952).

107. R. L. Stander (to U.S. Rubber), U.S. Pat. 2,598,077 (1952).

108. R. L. Stander (to U.S. Rubber), U.S. Pat. 2,598,078 (1952).

109. W. B. Reynolds (to Phillips Petroleum Co.), U.S. Pat. 2,658,876 (1953).

110. J. Thiele and K. Heuser, *Ann.* **290**, 30 (1896).

111. *BIOS Final Report 1729*, Item 22, p. 9.

112. A. W. Anderson (to Du Pont), U.S. Pat. 2,711,405 (1955).

113. G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *J. Am. Chem. Soc.* **82**, 5394 (1960).

114. A. W. Dox, *J. Am. Chem. Soc.* **47**, 1471 (1925).

115. C. E. H. Bawn and S. I. Mellish, *Trans. Faraday Soc.* **47**, 1216 (1951). F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.* **73**, 1691 (1951). D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.* **74**, 938 (1952). C. G. Overberger, *J. Polymer Sci.* **6**, 539 (1951).

116. M. Hunt (to Du Pont), U.S. Pat. 2,471,959 (1949). R. E. Burk (to Du Pont), U.S. Pat. 2,500,023 (1950). F. R. Mayo, F. M. Lewis, and C. Walling, *J. Am. Chem. Soc.* **70**, 1529 (1948).

117. J. M. DeBell, W. G. Joggin, and W. E. Gloor, *German Plastic Practice*, DeBell-Richardson, 1946, pp. 456–461. R. G. Stevens and H. G. Emblem, *Ind. Chemist* 391–394 (Sept. 1951). *India Rubber World* **124**, 716 (1951). *Rubber Age* **69**, 748 (1951).

118. *Plastics* **28** (306), 109 (1963).

119. H. Hardmann, *Rec. Trav. Chim.* **46**, 150 (1927).

120. R. A. Reed (to Whiffen & Sons, Ltd.), Brit. Pat. 808,763 (1959).

121. J. Thiele, *Ann.* **271**, 129 (1892).

122. T. Curtius, *Ber.* **26**, 405 (1893). J. M. Das-Gupta, *J. Indian Chem. Soc.* **11**, 207 (1934). T. H. Newby (to U.S. Rubber), U.S. Pat. 2,692,281 (1954).

123. *BIOS Final Report 1150*, p. 23; also Ref. 121.

124. L. Mehr (to Wallace & Tiernan, Inc.), U.S. Pat. 3,017,406 (1962).

124a. I. Binzer (to Fairmount Chemical Co.), Fr. Pat. 1,344,799 (1963).

125. H. A. Hill (to National Polychemicals, Inc.), U.S. Pat. 2,988,545 (1961).

126. *Brit. Plastics* **33** (10), 471 (1960).

127. J. Thiele, *Ann.* **270**, 9 (1892).

128. *Ber.* **46**, 2005 (1913).

129. L. Nass, *Mod. Plastics* **40** (7), 156 (1963).

130. "Genitron Blowing Agents," *Technical News*, Whiffen & Sons, p. 12.

131. W. B. Curtis and B. A. Hunter (to U.S. Rubber), U.S. Pat. 2,806,073 (1957).

132. G. M. Strongin and Ya. Yu. Rekminskii, U.S.S.R. Pat. 132,805 (1960).

133. R. A. Reed (to Whiffen & Sons), U.S. Pat. 2,804,435 (1957).

134. E. Mueller and S. Petersen, *Angew. Chem.* **63**, 18 (1951).

135. P. J. Flory, N. Rabjohn, and M. C. Shaffer, *J. Polymer Sci.* **4**, 435 (1949).

136. H. C. Marks, R. R. Joiner, and H. K. Parker (to Wallace & Tiernan, Inc.), U.S. Pat. 2,903,361 (1959).

137. *Federal Register*, July 18, 1962.

138. *Compounding Research Report No. 38*, Naugatuck Chemical Division, U.S. Rubber Co. Bulletin *PKB-1*, National Polychemicals, Inc. *Cellular Rubber*, Fisons Overseas Ltd.

139. R. J. Meyer and D. Esarove, *Plastics Technol.* **5** (3), 27 (1959). D. Esarove and R. J. Meyer, *Plastics Technol.* **5** (4), 32 (1959). D. J. Cram, M. Lavender, R. A. Reed, and A. Schoffield, *Brit. Plastics* **34** (1), 24 (1961). A. Warner, *Mod. Plastics* **9** (2), 135 (1961). H. A. Hackers, *Kunststoffe* **52** (10), 624 (1962). M. Lavender, *Plastics* **27** (299), 65 (1962).

140. H. R. Lasman, *SPE J.* **18**, 1184 (1962).

141. Th. Curtius and K. Heidenreich, *J. Prakt. Chem.* **52** (2), 476 (1895).

142. C. V. King, *J. Am. Chem. Soc.* **62**, 379 (1940).

143. M. J. Kleinfeld and B. A. Hunter (to U.S. Rubber Co.), U.S. Pat. 3,095,387 (1963).

144. H. A. Hill (to National Polychemicals), Brit. Pat. 916,352 (1963).

145. J. Thiele, *Ann.* **271**, 130, 133 (1893).

146. A. O. Rogers and M. A. Stevens (to Du Pont), U.S. Pat. 2,825,747 (1958).

147. Cogan and Barillet (to Et. Kuhlmann), Fr. Pat. 1,000,074 (1952).

148. R. B. Naylor (to Fisk Rubber Co.), U.S. Pat. 1,418,825 (1922).

149. L. C. Kulp, E. C. Van Buskirk, and B. A. Hunter (to U.S. Rubber), U.S. Pat. 2,621,161 (1952).

150. E. C. Soule (to Olin Mathieson), U.S. Pat. 2,832,744 (1958).

151. Th. Curtius and J. Thiele, *J. Prakt. Chem.* **44** (2), 161 (1887).

152. Van Gaver (to S.A. des Manufactures des Glaces et Produits Chimiques de Saint Gobain), U.S. Pat. 2,586,887 (1952; appl. made in France, April 30, 1948).

153. F. Loeber, M. Bogemann, and R. Wegler (to Farbenfabriken Bayer), Ger. Pat. 821,423 (applied April 6, 1949; issued Oct. 4, 1951); U.S. Pat. 2,626,933 (1953).

154. U.S. Rubber Co., Brit. Pat. 693,954 (applied Sept. 28, 1951; issued July 8, 1953).

155. Th. Curtius and F. Lorenzen, *J. Prakt. Chem.* **58**, 160–166.

156. A. A. M. Witte, *Rec. Trav. Chim.* **51**, 299–319 (1932).

157. R. A Reed, *Brit. Plastics* **33** (10), 472 (1960).

158. M. A. Albam and A. P. Pisarenko, *Kauchuk i Rezina* **18**, 9 (1959).

159. D. L. Schoene (to U.S. Rubber), U.S. Pat. 2,552,065 (1951). B. A. Hunter and D. L. Schoene, *Ind. Eng. Chem.* **44**, 119 (1952).

160. L. Clark, T. Grabowsky, and A. Poshkus (to Armstrong Cork Co.), U.S. Pat. 2,849,028 (1958). L. Clark (to Armstrong Cork), U.S. Pat. 2,873,259 (1959).

161. G. Wick, D. Homann, and P. Schmidt, *Kunststoffe* **49**, 383–390 (1959).

162. B. A. Hunter (to U.S. Rubber), U.S. Pat. 2,626,280 (1953).

163. B. A. Hunter (to U.S. Rubber), U.S. Pat. 2,673,220 (1954).

164. E. Dumont and H. Reinhardt, Ger. Pat. 1,001,488 (1957).

165. B. A. Hunter (to U.S. Rubber), Brit. Pat. 896,497 (1962; applied in U.S. on Dec. 31, 1959).

166. Wingfoot Corp., Brit. Pat. 719,102 (1954).

167. A. M. Clifford, S. W. Waisbrot, and G. H. Gates (to Goodyear Tire & Rubber Co.), U.S. Pat. 2,764,599 (1956).

168. R. A. Reed, "Modern Blowing Agents," *Plastic Progr.* **1955**, 67 (1956).

169. M. F. Fuller (to Du Pont), U.S. Pat. 2,732,353 (1956).

170. W. B. Hardy and F. H. Adams (to American Cyanamid), U.S. Pat. 2,863,866 (1958).

171. B. A. Hunter (to U.S. Rubber), U.S. Pat. 2,741,624 (1956).

172. J. B. Ott (to Monsanto), U.S. Pat. 2,518,249 (1950).

173. J. B. Ott (to Monsanto), U.S. Pat. 2,532,242 (1950).

174. J. B. Ott (to Monsanto), U.S. Pat. 2,532,243 (1950).

175. J. B. Ott (to Monsanto), U.S. Pats. 2,532,240 and 2,529,512 (1950).

176. K. L. Schmidt, F. Lober, E. Mueller, and H. Scheurlen (to Farbenfabriken Bayer), Ger. Pats. 1,102,384 and 1,116,391 (1961).

177. K. A. Jensen, *J. Prakt. Chem.* **159** (2), 191 (1941).

178. C. S. Argyle (to Whiffen & Sons), Brit. Pat. 801,825 (1958).

179. P. Griess and G. Harrow, *Ber.* **21**, 2737 (1888).

180. P. Duden and M. Scharff, *Ann.* **288**, 231 (1895).

181. F. Mayer, *Ber.* **21**, 2888 (1888).

182. G. Bourjol, *Mem. Poudres* **34**, 7 (1952).

183. H. Krzikalla, H. Pohlemann, and T. Toepel (to Badische), Ger. Pat. 1,004,618 (1951).

184. S. Ikuta and A. Nishimoto, *J. Soc. Rubber Ind. Japan* **28**, 270 (1955).

185. R. Kern, W. N. Grohs, and F. Blumel (to Rhein-Chemie), U.S. Pat. 2,891,017 (1959).

186. K. Vohwinkel and P. Stoecklin (to Farbenfabriken Bayer), U.S. Pat. 3,093,643 (1963; applied in Germany in 1959).

187. Imperial Chemical Industries Ltd., Indian Pat. 80,430.

188. H. L. Wunderly (to General Tire & Rubber), U.S. Pat. 2,666,751 (1954).

189. D. H. Lutz, *Report BL-301*, Elastomers Division, Du Pont, Wilmington, Del.

190. E. W. Hanson and D. R. Kuespert, *Report BL-253*, Rubber Chemicals Division, Du Pont, Wilmington, Del.

191. *Rubber Age* **61**, 340 (1947). *India Rubber World* **116**, 369 (1947).

192. M. F. Fuller (to Du Pont), U.S. Pat. 2,824,076 (1958).

93. E. Mueller, S. Petersen, and F. Loeblein (to Farbenfabriken Bayer), U.S. Pat. 2,683,696 (1954; applied in Germany in 1949).

94. R. A. Darrall and A. Lambert (to Imperial Chemicals Industries Ltd.), Brit. Pat. 822,976 (1959).

195. M. F. Fuller (to Du Pont), Brit. Pat. 753,879 (1956). M. F. Fuller, *Ind. Eng. Chem.* **49,** 722 (1957).

196. H. W. Bradley and M. F. Fuller (to Du Pont), U.S. Pat. 2,754,326 (1956).

197. C. B. Flack and E. R. Gray (to Du Pont), U.S. Pat. 3,055,846 (1960).

198. M. F. Fuller, *Ind. Eng. Chem.* **49,** 730 (1957). M. F. Fuller (to Du Pont), U.S. Pat. 2,776,265 (1957). *Plastics World*, PW 4641 (July 1961). R. M. Downing, R. E. Mortberg, and W. J. Smith (to Du Pont), U.S. Pat. 3,016,576 (1962).

199. C. S. Argyle and E. Vero (to Whiffen & Sons), Brit. Pat. 807,405 (1959).

200. I. A. V. Sullivan (to American Cyanamid), U.S. Pat. 2,960,481 (1960).

201. B. A. Hunter (to U.S. Rubber), U.S. Pat. 3,052,642 (1962).

202. R. L. Frank (to Ringwood Chemical Corp.), U.S. Pat. 2,676,928 (1954).

203. R. L. Frank (to Ringwood Chemical), U.S. Pat. 2,708,661.

204. C. C. Callis, F. W. Breuer, and L. L. Tolman (to Armstrong Cork Co.), Brit. Pats. 718,906 and 718,907 (1954). F. W. Breuer and L. L. Tolman (to Armstrong Cork), U.S. Pat. 2,744,076 (1956).

Henry R. Lasman
National Polychemicals, Inc.