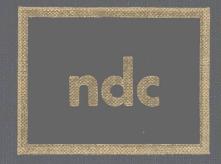
# Expanded Plastics and Related Products Developments Since 1978

CHEMICAL TECHNOLOGY REVIEW No. 221



# EXPANDED PLASTICS AND RELATED PRODUCTS

**Developments Since 1978** 

by

Yale L. Meltzer

NOYES DATA CORPORATION

Park Ridge, New Jersey, U.S.A.

1983

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### **Foreword**

The detailed, descriptive information in this book is based on U.S. patents, issued between January 1979 and June 1982, that relate to expanded and foamed plastics and related products. Our previous title *Foamed Plastics—Recent Developments* was published in 1976.

This book is a data-based publication, providing information retrieved and made available from the U.S. patent literature. It thus serves a double purpose in that it supplies detailed technical information and can be used as a guide to the patent literature in this field. By indicating all the information that is signicant, and eliminating legal jargon and juristic phraseology, this book presents an advanced commercially oriented review of recent developments in the field of expanded plastics and related products.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time.

Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The table of contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

#### 16 Reasons Why the U.S. Patent Office Literature Is Important to You

- The U.S. patent literature is the largest and most comprehensive collection
  of technical information in the world. There is more practical commercial process information assembled here than is available from any other
  source. Most important technological advances are described in the patent literature.
- The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
- The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
- An important feature of the patent literature is that it can serve to avoid duplication of research and development.
- Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
- It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
- 7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
- 8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
- Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
- Obtain licenses—many U.S. chemical patents have not been developed commercially.
- 11. Patents provide an excellent starting point for the next investigator.
- 12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
- Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
- 14. Identifying potential new competitors.
- 15. It is a creative source of ideas for those with imagination.
- 16. Scrutiny of the patent literature has important profit-making potential.

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# Introduction Product and Market Information

#### PRODUCT CLASSIFICATION

Expanded plastics are also called "foamed plastics" or "cellular plastics." Expanded plastics can be flexible, semi-flexible, semi-rigid or rigid. They can also be thermoplastic or thermosetting and can exist as open-celled or closed-celled materials.

#### INDUSTRIAL PERSPECTIVES

For 1981, the U.S. Federal Trade Commission has found the following results for the "Chemicals and Allied Products Industries" (Table 1.1):

Table 1.1: Sales and Net Income, Chemicals and Allied Products
Industries, 1979–1981
(in millions of dollars, except as noted)

| Year  | Sales (\$) | Net<br>Income (\$) | Percent<br>Return (%) |
|-------|------------|--------------------|-----------------------|
| 1979  | 149,181    | 10,896             | 7.3                   |
| 1980  | 162,390    | 11,219             | 6.9                   |
| 1981* | 183,000    | 11,300             | 6.2                   |

<sup>\*</sup>Based on six months' data.

Source: U.S. Federal Trade Commission

A component of the "Chemicals and Allied Products Industries" (Standard Industrial Classification, SIC 28) is the "Plastics Materials and Resins Industry" (SIC 2821). In addition, there is the "Plastics Products Industry" (SIC 3079). Accord-

ing to the U.S. Department of Commerce, the value of shipments of plastics materials and resins rose only 6.3% in real terms (based on 1972 dollars) in 1981 over 1980. This results from the value of shipments (in 1972 dollars) being estimated at \$5,270 million for 1980 vs \$5,600 million for 1981 (see Table 1.2).

Estimates by the U.S. Department of Commerce place the value of shipments (in real terms, based on 1972 dollars) by the "Plastics Materials and Resins Industry" at 6.7% for 1982 over 1981. The value of shipments for 1982 is estimated to be \$5,975 million for 1982 compared to \$5,600 million for 1981 (see Table 1.2).

Most plastics materials and resins are sensitive to general economic conditions, but some are more sensitive than others. Product shipments of plastics materials and resins were 8% lower in 1980 than in 1979 (in 1972 dollars), \$5,965 million for 1980 vs \$6,487.3 million for 1979. Sales in 1981 were slow as a result of softened demand in domestic U.S. markets (e.g., automobile and housing markets), which together consume 25% of the output of plastics materials.

The plastics materials and resins industry is capital-intensive. Expenditures for new facilities and equipment amounted to more than \$1,000 million in 1979. Employment, estimated at 53,500 in 1981, has not varied substantially in size in recent years, although employment was particularly high in 1979, when it reached 60,300.

Capacity utilization in 1981 suffered, although production was 5% higher than in 1980. Actual capacity utilization in 1980 ranged from 70% for PVC to 77% for high density polyethylene (HDPE). In contrast, 1979 capacity utilization was 84% for PVC and 89% for HDPE. Total production of plastics materials and resins, according to the U.S Department of Commerce, reached a record 41,900 million pounds in 1979, but fell 9% in 1980.

The product price index for plastics materials and resins rose by 17.6% in 1979, by 17.9% in 1980 and by about 6% in 1981 mainly due to higher costs for feed-stocks, energy and capital. The weak markets for plastics materials in 1981 prevented producers from passing on costs to consumers. Some producers sold at discounts just to maintain their market shares.

In 1981, there was an export decline. The European Community has claimed that price controls on petroleum and natural gas have given U.S. producers a cost advantage. The 1981 U.S. export decline served to mitigate this issue.

Plastics manufacturers in the European Community had to reduce prices, as did U.S. manufacturers, as a result of overcapacity and reduced demand. Japanese manufacturers are also attempting to bring output into line with demand.

According to the U.S. Department of Commerce, R&D expenditures by the plastics industry will continue to be higher than the average of about 3% of sales for the overall chemicals and allied products sector.

285 0.122 0.014

0.147 263.4

0.129 246.4

215.7 0.092 0.015

106.3 0.087 0.009

56.4 0.098

Table 1.2: Plastics Materials and Resins (SIC 2821): Trends and Projections 1972-82 (in millions of dollars except as noted)

| * *  |                     |                        |                          |                         |                      | :       |                      |                                 |                                  |                                | :     |                  |                  |
|--|---------------------|------------------------|--------------------------|-------------------------|----------------------|---------|----------------------|---------------------------------|----------------------------------|--------------------------------|-------|------------------|------------------|
| Percent<br>Change<br>1981-82***                    | 11                  | 3.0                    | 0.9                      | 6.3                     | 1                    |         | 1                    | 6.5                             | 1                                | 6.3                            |       | 15.1             | 5.3              |
| 1982***  | 1 11                | 55.6                   | 33.6                     | 11.50                   | 1                    |         | ı                    | 6,750                           | 1                                | 42,500                         |       | 2,900            | 300              |
| Compound<br>Annual<br>Rate of<br>Growth<br>1972-81 | 1 11                | -0.3                   | -1.1                     | 9.0                     | 1                    |         | 1                    | 3.9                             | 14.1                             | 4.9                            |       | 1                | 1                |
| 1982**   | 17,500              | 53.5                   | 31.7                     | 10.82                   | 1                    |         | 20,720               | 6,340                           | 326.8                            | 40,000                         |       | 2,520            | 285              |
| 1980*  | 15,570              | 58.0                   | 35.7                     | 9.84                    | 1                    |         | 18,390               | 5,965                           | 308.3                            | 38,100                         |       | 2,703.4          | 263.4            |
| 1979<br>Data                                       | 14,282.4            | 60.3                   | 38.4                     | 8.86                    | 1,077.1              | Data    | 16,964.2             | 6,487.3                         | 261.5                            | 41,871                         |       | 2,183.3          | 246,4            |
| 1978<br>Industry                                   | 11,997.5            | 57.6                   | 36.9                     | 8.28                    | 972.4                | Product | 13,783.1             | 6,197.4                         | 222.6                            | 38,878                         | Trade | 1,268.3          | 215.7            |
| 1977   | 10,818.2            | 57.2                   | 36.7                     | 7.52                    | 895.2                |         | 12,181.1             | 5,546.9                         | 219.6                            | 34,623                         |       | 1,057.2          | 106.3            |
| 1972   | 4,478.2             | 54.8                   | 35.0                     | 4.98                    | 253.2                |         | 4,486.4              | 4,486.4                         | 100.0                            | 25,921                         |       | 438.9            | 56.4             |
| Item   | Value of shipments† | Total employment (000) | Production workers (000) | production workers (\$) | Capital expenditures |         | Value of shipments†† | Value of shipments (1972 \$) †† | Product price index (1972 = 100) | Quantity produced (million lb) |       | Value of exports | Value of imports |

Note: Estimates and forecasts by the U.S. Bureau of Industrial Economics.

Import/new supply ratiot11 Export/shipments ratio

\*Estimated except for product price index, exports, and imports.

\*\* Estimated. \*\*\* Forecast.

†Value of all products and services sold by industry SIC 2821.

t Value of shipments of plastic materials, synthetic resins and nonvulcanizable elastomers produced by all industries. †††New supply is the sum of product shipments plus imports. Sources: U.S. Bureau of the Census; U.S. Bureau of Industrial Economics and U.S. Department of Commerce

Over the years, revised housing codes have stimulated the use of rigid plastics for pipe and fittings, making this application in construction one of the plastic industry's faster growing areas. Furniture manufacturers are using more plastics (e.g., PVC and foamed polystyrene) for upholstery and molded shapes and as substitutes for wood. The automobile industry is relying more and more on plastics materials to decrease car weights in order to increase miles per gallon of fuel.

EPA, FDA, OSHA and CPSC (Consumer Product and Safety Commission) regulations, that limit exposure to proven and suspected carcinogens, will raise producer costs by requiring new ventilation and protective systems. For example, the CPSC 4-to-1 vote in February 1982 to ban the use of urea-formaldehyde foam insulation in schools and homes in the United States will certainly have profound effects on the expanded plastics (foams) industry. Use of urea-formaldehyde foam insulation has actually sharply declined since 1977, with a particularly low level of use in 1981 and 1982.

One problem that the industry has been coping with quite well, however, is that of water disposal from processing plants. More difficult problems are those connected with disposal of increasing amounts of plastics products in municipal dumps.

Dealing with flame retardance and reduced smoke emissions of plastics materials and products has become a major concern for the plastics industry. The industry has to meet strict standards. This has been and will continue to be a major concern for the foreseeable future.

#### STATISTICAL CLASSIFICATIONS

In an attempt to more adequately analyze the plastics industry, the U.S. Department of Commerce has created a new category: the miscellaneous plastics products industry. This category is a residual statistical creation encompassing plastics products not reported in other industries or not consumed within the companies that produce them,

Seven major product groups (markets or processes) account for almost 75% of the value of shipments of plastics products. These are: (1) film and sheeting, (2) consumer and commercial products, (3) packaging, (4) building and construction products, (5) transportation products, (6) electrical and electronic products and (7) laminated products. The industry accounts for approximately half of the total consumption of plastics and resins in the United States (see Table 1.3).

Table 1.3: Plastics Product Shipments by Class

|                   | Shipments (millions of 1972 \$) |         | Compound Annual<br>Growth Rate |   |
|-------------------|---------------------------------|---------|--------------------------------|---|
| Product Class     | 1972                            | 1978    | (%)                            |   |
| Film and Sheeting | \$2,065                         | \$2,706 | 4.6                            |   |
| Foamed Plastics   | 878                             | 912     | 0.6                            |   |
|                   |                                 |         | (continued                     | d |

Table 1.3: (continued)

|                         | Shipments (millions of 1972 \$) |       | Compound Annual<br>Growth Rate |
|-------------------------|---------------------------------|-------|--------------------------------|
| Product Class           | 1972                            | 1978  | (%)                            |
| Laminated Sheets        | 568                             | 873   | 7.4                            |
| Packaging               | 1,271                           | 1,668 | 4.6                            |
| Industrial Products     | 1,820                           | 2,030 | 1.8                            |
| Construction Products   | 1,115                           | 2,019 | 10.4                           |
| Dinnerware, Tableware   | 377                             | 446   | 2.8                            |
| Regenerated Cellulose   | 429                             | 191   | -7.6                           |
| Custom Compounds        | 227                             | 385   | 9.2                            |
| Consumer and Commercial | 2,344                           | 4,913 | 13.1                           |

Sources: U.S. Bureau of the Census; U.S. Bureau of Economic Analysis; and

U.S. Department of Commerce

As of 1982, the new Standard Industrial Classification (SIC) system will replace SIC 3079 (plastics products industry) with six new industries. These are:

| SIC Number | Description  |
|------------|--|
| 3071       | Plastics film and sheet                            |
| 3072       | Plastics pipe and conduit                          |
| 3073       | Plastics bottles                                   |
| 3074       | Plastics foam products                             |
| 3076       | Molded plastics products, not elsewhere classified |
| 3078       | Miscellaneous plastics products                    |
|            |  |

#### **FUTURE PROSPECTS**

In the future, substitution of expanded plastics (or foamed plastics) for natural products, such as metal and wood, can be expected to continue. Competition between expanded plastics and natural products, however, should become less intense, while competition among the expanded plastics themselves for markets should become more intense. Likewise, increased competition of different types of plastics should increase. An increased emphasis on R&D will be necessary for companies to protect their market shares or to expand.

According to the U.S. Department of Commerce, feedstock shortages are not expected, although the plastics industry has sometimes had difficulty obtaining all the petroleum and natural gas that it has needed. Although only an estimated 1.5% of domestic consumption of these raw materials is used to make plastics, preference has been given to heating and energy uses. The need for a long-term raw materials base has led to mergers and acquisitions, such as the DuPont-Conoco merger. Producers that are not integrated or do not have steady access to feedstocks may find themselves at a disadvantage in meeting the growing domestic and overseas competition.

## **Polyamides and Polyimides**

#### **POLYAMIDES**

#### **High Impact Polyamides**

Highlights of the Technological Achievement: A high impact polyamide composition is disclosed which comprises at least 50% of a polyamide resin having a relative viscosity of at least 4.0, 5 to 30% of an olefin-acid copolymer, ionomers thereof, or mixtures of these, and 5 to 30% of a stabilizing polyamide resin which contains at least one long-chain amide-forming monomer component.

Reference: D.E. Stewart; U.S. Patent 4,299,744; November 10, 1981; assigned to American Hoechst Corporation.

**Background:** Although the polyamides in general use today such as nylon 6, nylon 6,6 and the various nylon copolymers are desirable for most applications, there are many specialty applications such as automotive and machinery parts which require exceptional strength and toughness.

Various attempts have been made to increase the impact strength of polyamides. A common technique involves the formation of polyamide compositions containing olefin/carboxylic acid copolymers or ionomers (olefin/acid copolymers wherein a portion of the acid groups are neutralized with metal ions).

**Process Conditions:** The high impact polyamide composition provided by this process comprises:

- (a) at least 50% of a polyamide resin having a relative viscosity of at least 4.0 measured as a 1% solution in sulfuric aicd at 25°C;
- (b) 5 to 30% of an impact modifier selected from the group consisting of:

- (1) an olefin-acid copolymer comprising at least 50 mol % based on the copolymer of an  $\alpha$ -alkene having 2 to 10 carbon atoms, or mixtures of such  $\alpha$ -alkenes, and 0.2 to 25 mol % based on the copolymer of an  $\alpha,\beta$ -ethylenically unsaturated carboxylic acid having 3 to 8 carbon atoms, mixtures of such acids, or the salts, esters or anhydrides thereof;
- (2) ionomers of the olefin-acid copolymers defined in (1) wherein at least 10% of the carboxylic acid groups are neutralized with metal ions; and
- (3) mixtures of (1) and (2); and
- (c) 5 to 30% of a stabilizing polyamide resin which contains at least one long-chain amide-forming monomer component having at least 9 atoms separating the amide-forming sites of the monomer.

Suitable long-chain amide-forming monomers include the polyether diamines having the formulas:

wherein a is 2.6 to 35 and

wherein c is 10 to 50 and b + d is 2 to 5. Preferred are the polyether diamines having a molecular weight of 400 to 600.

**Example:** A pellet tumble blend of the following components were charged to a 1.75", 20/1 L/D, Essex extruder and extruded at a temperature profile of 450°F (rear), 525°F (mid), 525°F (front) and 525°F (die) through a 20-60-150 mesh screenpack.

| Components  | Parts by Weight |
|---|-----------------|
| Polycaprolactam*  | 69.75           |
| Ethylene/ethyl acrylate copolymer (Union Carbide DPDA-9169)**       | 5.00            |
| Ionomer of ethylene/methacrylic acid copolymer (Dupont Surlyn 1856) | 10.00           |
| Lubricant   | 0.25            |
| Copolymer of caprolactam (85%) and aminoundecanoic acid (15%)***    | 15.00           |

<sup>\*</sup>Relative viscosity ~5.0 measured as 1% solution in H<sub>2</sub>SO<sub>4</sub> at 25°C.

<sup>\*\*</sup>Containing 18% ethyl acrylate.
\*\*\*Having a relative viscosity of ~3.4 (1% solution in m-cresol at 25°C).

The substantially homogeneous composition was water quenched, pelletized and externally lubricated.

#### Flameproof Polyamide Molding Compositions

Highlights of the Technological Achievement: Self-extinguishing, flameproved, reinforced and/or filled polyamide molding compositions containing as flame-proofing agents a combination of a phenol-aldehyde resin and an alkali metal-or ammonium-polyphosphate.

**Reference:** P. Tacke, D. Neuray and D. Michael; U.S. Patent 4,244,858; January 13, 1981; assigned to Bayer AG, Germany.

**Background:** Combinations of halogen compounds and synergistically acting metal compounds respectively powder-form red phosphorus are widely used as flameproofing agents for glass-fiber-reinforced or mineral-filled polyamide molding compositions.

The main disadvantage of using red phosphorus as a flameproofing agent is that the powdered red phosphorus is difficult to handle because, in the presence of air, it shows a tendency towards dust explosions on coming into contact with hot metal surfaces under conditions of the kind generally encountered in the machines normally used for producing and processing the molding compositions.

**Process Conditions:** It has been found that alkali metal and/or ammonium polyphosphate in combination with phenol-aldehyde resins have an excellent flame-proofing effect on reinforced and/or filled polyamide molding compositions, enabling them to comply with the requirements for Fire Classes VO according to UL (Underwriters' Laboratory).

This synergism is particularly surprising because the phenol-aldehyde resins themselves are readily inflammable, require a flameproof finish to reduce their inflammability and also have no significant effect on their own as flameproofing agents in polyamide molding compositions.

Because all the components of this flameproofing agent combination are substantantially colorless or white, it is possible to obtain VO-rated (according to UL) polyamide molding compositions in light colors which do not have any of the disadvantages referred to above.

This process relates to self-extinguishing molding compositions comprising:

- (1) preferably 50 to 80% by weight of polyamide;
- (2) preferably 2 to 15% by weight of alkali metal and/or ammonium polyphosphate;
- (3) preferably 2 to 15% by weight of phenol-aldehyde resin, and
- (4) preferably 15 to 35% by weight of reinforcing materials and/or fillers, the sum of components (1) through (4) having to amount to 100% by weight.