

# ACRYLONITRILE

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**a TECHNOMIC<sup>®</sup> publication**  
**TECHNOMIC Publishing Co., Inc.**  
**265 W. State St., Westport, Conn. 06880**

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*Progress in Materials Science Series . . . Volume VI*

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265 W. State St., Westport, Conn. 06880

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PRINTED IN U.S.A.

Library of Congress Card No. 75-125403  
Standard Book No. 0-87762-050-4

## PREFACE

Two unusual features of this monograph on acrylonitrile deserve comment. They are the extent of coverage given to the production of acrylonitrile, and the citing of more than 200 publications from the Soviet literature.

Better than two-thirds of the text, and three-quarters of the references cited, relate to the formation and commercial production of acrylonitrile. Not unexpectedly, the major emphasis is directed to the process known as the oxidative ammonolysis of propylene, the process chosen for the manufacture of acrylonitrile in the USSR. Much of the cited Soviet research is concerned with the catalysis and reaction kinetics of this process. However, it is apparent that both the gas and liquid-phase modifications of the acetylene-hydrogen cyanide process were also investigated by Soviet scientists. Curiously, no figures are shown for existing or projected acrylonitrile capacity in the USSR, or for requirements for acrylonitrile and its copolymers.

The remainder of the monograph is concerned with the chemical properties and applications of acrylonitrile. In the former section, discussion of some areas of acrylonitrile chemistry, notably the chemistry of the nitrile group, and of cyanoethylation and de-cyanoethylation reactions, is comparatively brief. The authors explain their decision, however, by referring to four Russian reviews covering these areas.

The citations from the Soviet literature must be considered a strong point. It is likely that most of these articles, published since 1960, have not been previously quoted in English. They will undoubtedly provide stimulation to those concerned with the production, chemistry and applications of acrylonitrile.

Dr. Gingold has taken some pains to retain the flavor of the Russian text. To this end, his changes from the original wording have been limited to corrections of what were almost certainly errors in transcription, typesetting or editing of the original Russian text.

Richard P. Welcher  
October 1970

## TRANSLATOR'S PREFACE

Probably the most valuable part of the present monograph is the bibliography of over 1400 references. However, a simple inspection of this bibliography showed that it contained numerous errors and duplications. A determined effort was therefore made to correct the errors and point out the duplications wherever possible. Some additional comments on this point are made in a footnote at the start of the bibliography.

Changes in nomenclature have been made to ensure its intelligibility to the reader, and errors in formulas and equations have been corrected.

I am grateful to Miss Barbara M. Allstrom for help with the nomenclature, to Miss Carole C. Coggnetta for typing the manuscript, and to Mrs. Judith Kagan and Mrs. Elisabeth C. Whiton for their assistance in checking the bibliography.

Kurt Gingold  
October 1970

## FOREWORD

In recent years, the industrial production of acrylonitrile has undergone significant development. The development of the process of oxidative ammonolysis of propylene has caused a rapid increase in the capacity for acrylonitrile production in all countries with a developed petrochemical industry. This has also led to the development of industries using acrylonitrile: New synthetic fiber plants have been established, and there has been an increase in the capacity for the production of nitrile rubber, acrylonitrile-butadiene-styrene copolymers, and the like.

In the Soviet Union, the industrial production of acrylonitrile from ethylene oxide and from acetylene has been adopted. In the coming years, plants for the production of acrylonitrile from propylene and ammonia will be set up.

Acrylonitrile is used on an industrial scale in the Soviet Union for the production of various synthetic fibers, nitrile rubber, polyacrylamide, polyelectrolytes, and a number of other products.

The reduction in the price of acrylonitrile brought about by the development of the oxidative ammonolysis of propylene has aroused considerable interest in this product on the part of synthetic chemists.

The combination of the economic factor and the high reactivity of acrylonitrile has ensured the rapid expansion of its area of industrial application. An excellent illustration of this is the process for the conversion of acrylonitrile to adiponitrile, which leads to the partial replacement of benzene by propylene in such an important field of petrochemistry as the production of polyamides.

The purpose of the present monograph is to correlate the huge amount of factual material on the industrial chemistry of acrylonitrile, particularly with respect to its production and new areas of application. Unfortunately, it has not been possible to cover all of the material. Most of the material used was published up to the middle of 1966.

In conclusion, the authors express their deep gratitude to Dr. L. Ya. Margolis and to Mr. V. A. Yanshevskii, Chief Engineer of the Novokuibyshev branch of the State Planning and Scientific Research Institute of the Synthetic Rubber Industry, for discussing the manuscript of this book, and also to their co-workers A. R. Madera, L. S. Akimova, T. Ya. Gusman, and others, for helping with the preparation of the manuscript for publication.

## INTRODUCTION

Acrylonitrile - the nitrile of acrylic acid, or vinyl cyanide - was discovered at the end of the nineteenth century, but did not find practical application until the 1930s, after it had been found that the butadiene-nitrile rubber prepared from it is highly resistant to swelling in gasoline, oils, and many other solvents. The production of this type of synthetic rubber was started in Germany and continued up to the end of World War II. A similar production was started at almost the same time in the United States.

Theoretical considerations provided a basis for suggesting the possibility of preparing synthetic fibers with extremely valuable properties from an acrylonitrile polymer. Polyacrylonitrile (PAN) fibers can be prepared only by formation from solution, since PAN decomposes below its melting point upon heating.

However, it took a long time to find a solvent for PAN. Not until 1942 did Rein and Houtz find, almost simultaneously, that dimethylformamide can be used for this purpose [1, 2].

In 1944, polyacrylonitrile fiber was prepared for the first time in an experimental plant in Waynesboro, Virginia, and in 1950 the Du Pont Company manufactured commercial samples of this fiber under the trademark Orlon.

Since that time, the requirements for acrylonitrile have been increasing continuously. The rate of this increase has required improvements in the technology for its production and the search for new methods of synthesis. In the first plants, acrylonitrile was prepared from ethylene cyanohydrin, by a method proposed by Moureu as early as 1893. This process was later replaced by a "direct" synthesis from acetylene and HCN.

After 1960, the production of acrylonitrile received a new powerful impulse as a result of the development of a process for the oxidative ammonolysis of propylene.

The dynamic growth of acrylonitrile production in the United States and Japan is shown by the data presented in Figure 1.

The acrylonitrile requirements in the United States in 1963 and those predicted for 1968 [3] are shown in Table 1.

As can be seen, first place in acrylonitrile requirements is occupied by acrylic fiber production. Strictly speaking, acrylic fibers contain more than 85 weight % of acrylonitrile. However, modified acrylic fibers with acrylonitrile contents of 35-85% are also produced, which are copolymers of acrylonitrile with other vinyl monomers: vinyl chloride, vinyl acetate, vinylpyrrolidone, vinylidene chloride, and others.

Acrylic fibers are superior to all other synthetic fibers in light stability, are characterized by elasticity and a wool-like appearance, and are suitable for use in mixtures with wool. They are used for the production of apparel fabrics, staple fiber, carpets, cord fabrics, and other purposes. The production of acrylic fibers in the capitalist countries amounted to 3000 tons\* in 1950, 28,000 tons in 1955, 129,000 tons in 1960, and 215,000 tons in 1963. An output of 329,000 tons was expected for 1965. [4, 5, 7].

The production of acrylic fibers in the United States was 84,000 tons in 1963, 127,000 tons in 1964, and 158,000 tons in 1965. It was expected that the production of acrylic fibers in the United States would reach 230,000 tons in 1970.

Acrylonitrile fibers in the United States are produced by the Du Pont Company (Orlon), Monsanto Company (Acrilan), American Cyanamid Company (Creslan), Dow Chemical Company (Zefiran), Eastman Kodak Company (Verel), and Union Carbide Corporation (Dynel) [6].

The production of acrylic fibers in Western Europe is less developed than in the United States [8]. However, plants are known to be operating in England [9], West Germany, France, and Italy [10], and in the Netherlands [11]. There is a large-scale production of acrylic fibers in Japan (capacity about 100,000 tons in 1965) [10, 11, 29].

About 30% of the world's output of acrylic fibers is used in the production of sweaters and blankets, 20% is used for knitted fabrics, and 16% for carpet production [7].

Second place in acrylonitrile requirements is occupied by the plastics industry. Polyacrylonitrile itself is not used as a plastic because of forming problems. However, copolymers of acrylonitrile with styrene and butadiene are widely used, and their production is increasing rapidly. In the United States, for example, the annual increase in the production of acrylonitrile-butadiene-styrene (ABS) resins was 35-38% in the period 1963-1965 [29].

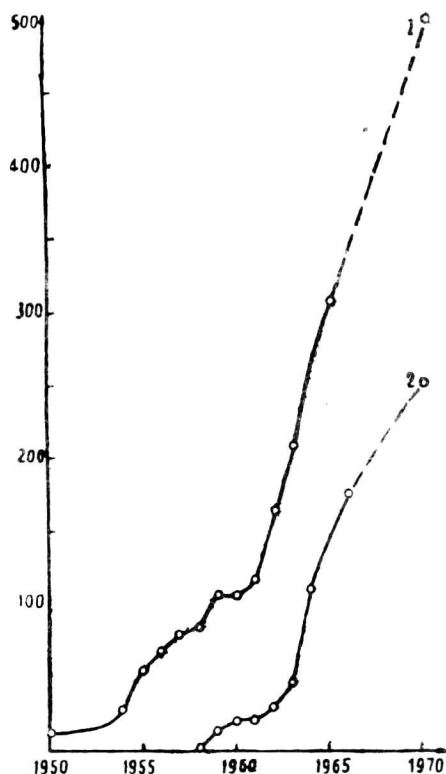
Acrylonitrile-styrene copolymers have a higher impact strength, higher softening point, and greater solvent resistance than polystyrene.

ABS resins have a high heat resistance and stability toward corrosive media.

---

\* The units are metric tons (1 metric ton = 1000 kg).





**Figure 1.** Volume of acrylonitrile production (thousands of tons per year):

1. United States; 2. Japan

They operate successfully, when at temperatures between  $-40$  and  $+105$  degrees C and are therefore widely used for the production of pipes for carrying hot water and some corrosive products, as a lining material for refrigerators, and in the automotive industry [13].

Table 1

Acrylonitrile Requirements in the United States

	1963		1968	
	Thousands of tons	%	Thousands of tons	%
Production of acrylic fibers	82.2	50.8	124.7	52.4
Production of acrylonitrile-styrene copolymers	15.9	9.8	43.1	18.1
Production of nitrile rubber	13.6	8.5	18.1	7.6
Other uses	20.4	12.6	36.2*	15.2
Export	29.5 (90)	18.3	15.9	6.7
Total	161.6	100	238	100

\*It is possible that about 100,000 tons of acrylonitrile, in addition to the quantity indicated, will be processed to adiponitrile.

Summary of Data on the Production Capacity  
for Copolymers Outside the Soviet Union [14-20]

Country	Company	Capacity (thousands of tons/ year)
U.S.A.	Naugatuck Chemical Co.	72.6 (1961)
	Marbon Chemical Co.	106.0 (1963)*
	B. F. Goodrich Chemical Co.	
	Monsanto Chemical Co.	
Great Britain	Distillers Co.	
	Marbon Chemical Co.	16.0 (1964)
	Stow Chemical Co.	
	Monsanto Chemical Co.	
West Germany	BASF	
	Farbenfabriken Bayer	Not known
	Chemische Werke Hüls	
Italy	Soc. Edison S.p.A.	
	ANIC S.p.A.	above 11.0 (1964)
	Soc. Italiana Resine S.p.A.	
	Mazzucchelli Celluloide S.p.A.	
Japan		36.0** (1964)
Canada	Monsanto Canada	
	Polymer Corporation	1.8 (1964)

\*These figures may be high. According to another source [29], the production of ABS resins in the United States was 45,400 tons in 1963, 59,000 tons in 1964, and 79,400 tons in 1965.

\*\*According to the data of [781], 6500 tons of acrylonitrile was used in the production of ABS resins in Japan in 1965.

The consumption of ABS resins in the United States in 1965 was as follows [21]:

Articles prepared by casting under pressure	39 %
For automotive use	12 %
Articles prepared by extrusion	13.0%
Piping	10.3%
Sheet materials for refrigerators	42.7%
Blown articles	4.8%
Total	100%

In Japan, ABS resins are used as follows [21] :

Automotive industry	30%
Instrument making	30%
Footwear, helmets, etc.	15%
Mixed with other materials	<u>25%</u>
Total:	100%

Acrylonitrile-styrene copolymers are used for the production of storage-battery cases and in transport machine building.

Although the production of nitrile rubber was the first industrial application of acrylonitrile, it is now only in third place in the consumption of this chemical. This does not mean that the production of nitrile rubbers has decreased; up to the present, nitrile rubber has been in first place in volume of production among the special grades of synthetic rubber.

In 1965, the nitrile rubber production capacity in the capitalist countries was close to 162,000 tons/year [22], including 85,500 tons/year in the United States [23], 25,000 tons/year in West Germany (Farbenfabriken Bayer) [24], 10,000 tons/year in France (Ugine) [25], 12,400 tons/year in Italy (ANIC, Montecatini) [26], and 10,000 tons/year in Japan [781].

About 30% of the nitrile rubber produced in the United States is used in the production of rubber goods. A considerable part of the output (36.5%) is used by the paper, leather, and textile industries [27].

As can be seen from the data above, a vigorous growth in the production and consumption of acrylonitrile has been observed during recent years. This is related to two factors. First, materials made from acrylonitrile (fibers, plastics, etc.) have enjoyed good sales, as a result of their valuable use properties. Second, starting in 1960, a process for the production of acrylonitrile from propylene has been used industrially. This process has good technical and economic characteristics [30], leading to a considerable reduction in the price of acrylonitrile.

A comparison of the technical-economic characteristics for the production of acrylonitrile from acetylene and propylene is given below:

Characteristic	Production from acetylene (%)	Production from propylene (%)
Specific capital investment for items for fundamental industrial purposes:		
a) for the production of acrylonitrile alone	100	165

b) including related capital investments for the production of raw materials and intermediates	289	216
Cost of acrylonitrile	\$100	\$ 63

The above data show that a changeover to the production of acrylonitrile from propylene results in a 25% decrease in the specific capital investment for production (including related expenses) and in a 37% reduction of the net cost of commercial production.

In 1961, after the start-up of plants for the production of acrylonitrile from propylene, the price of acrylonitrile on the world market dropped from \$305 per ton [28] to \$320 per ton. This opened the way for the industrial realization of some new synthesis based on acrylonitrile. The most important of these is the process for the reductive dimerization of acrylonitrile to adiponitrile, which is a raw material for the production of Nylon 66. This synthesis will probably become one of the main uses for acrylonitrile in the near future. Among other uses of acrylonitrile that are of definite interest from the practical point of view, the production of methyleneglutaronitrile, polyelectrolytes, acrylamide, acrylic acid and its esters, and of a number of plasticizers, herbicides, and the like should be noted.

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## CHAPTER I

### SURVEY OF REACTIONS LEADING TO THE FORMATION OF ACRYLONITRILE

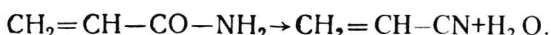
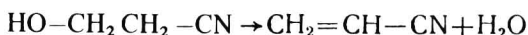
Four methods for the production of acrylonitrile are of practical importance at present:

1. Dehydration of ethylene cyanohydrin.
2. Direct addition of HCN to acetylene in the liquid phase.
3. Direct addition of HCN to acetylene in the gas phase.
4. Combined oxidation of propylene and ammonia.

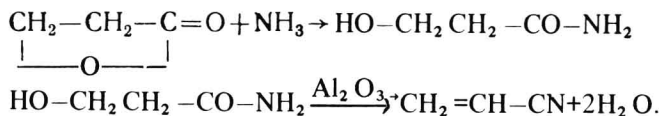
An analogy to the first of these processes was the method for the thermal dehydration of lactonitrile developed in Germany (Knapsack process). A modification of the last process for the production of acrylonitrile is the DuPont process, based on the reaction of nitric oxide with propylene.

Since all four methods are of great interest, special sections of the present monograph will be devoted to their examination. However, there are many other reactions which, although not of industrial significance at this time, also lead to the formation of acrylonitrile. A brief survey of presently known reactions leading to the formation of acrylonitrile is given below.

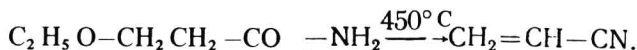
In 1893, Moureu established the structure of acrylonitrile, which he prepared by the removal of water from ethylene cyanohydrin and by the dehydration of acrylamide in the presence of phosphorus pentoxide [31, 32]:



In 1945, Kung prepared acrylonitrile by the catalytic dehydration of acrylamide, by passing its vapor over pyrolusite heated to 490-500 degrees C. The yield of acrylonitrile was 67% [33]. In a similar way, two molecules of water can be removed in one stage from beta-hydroxypropionamide [34], which in turn can be prepared in 50% yield from the corresponding lactone by reaction with excess liquid ammonia:



It is possible to remove a molecule of alcohol from beta-alkoxypropionamide (or beta-alkoxyisobutyramide) in the presence of silica containing a small amount of tantalum, zirconium, or tungstic oxide [35]:



### Acrylonitrile

Another dehydration reaction leading to the formation of acrylonitrile is the cleavage of water from aldoximes. The most frequently used dehydrating agent is acetic anhydride. Acrylonitrile is formed almost quantitatively from acrolein oxime by this method [36, 37].

Acrolein oxime is obtained by passing propionaldehyde oxime over a mixed catalyst (bauxite/chromic oxide) at a temperature of 400-500 degrees C [38, 39].

According to a series of U.S. patents [40-42], acrylonitrile is obtained by the dehydrogenation of propionitrile:

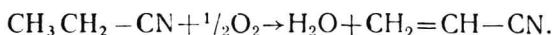


The dehydrogenation is carried out at 600-625 degrees C in the presence of chromium and vanadium oxides. This reaction proceeds with better results over tungsten and nickel sulfides at a quite high temperature [43] or over a molybdenum catalyst [44].

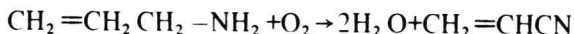
Acrylonitrile is also obtained by the dehydrogenation of allylamine [45]:



The oxidation of propionitrile by atmospheric oxygen in the gas phase leads to exactly the same result as its dehydrogenation. The catalyst for the oxidation process is finely ground copper or silver, and the reaction is facilitated by the addition of 2% of iodine [46] or hydrogen bromide [47]. In the presence of iodine, the degree of conversion is 25% and the yield 80-85%. The process is carried out at a temperature of 600-610 degrees C:



Acrylonitrile is also obtained by the catalytic oxidation of allylamine [48]. The reaction is carried out in the presence of water vapor at 450-600 degrees C over silver deposited on silicon carbide:

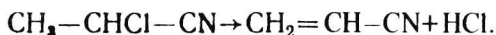


The yield of the desired product is 90%, and ammonia, carbon dioxide, acetone, and HCN are also formed.

Unsaturated nitriles are obtained by the removal of a molecule of hydrogen chloride from chlorinated saturated nitriles in the liquid phase in the presence of tertiary bases, such as pyridine [49, 50]. The dehydrohalogenation is carried out at a temperature of 150-250 degrees C.

The removal of hydrogen chloride from alpha-chloropropionitrile is best accomplished by a catalytic method in the gaseous phase [51]. Titanium dioxide [52-55], ferric chloride [56], or the hydrochloride of an organic base [57] is used as catalyst:

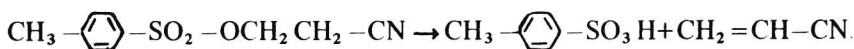




The process temperature is 575-625 degrees C. If the reaction is carried out in the presence of methanol, methyl chloride is obtained instead of hydrogen chloride [57].

Acrylonitrile is also obtained by the decomposition of ethylene cyanohydrin ethers and esters. Thus, for example, the methyl ether of ethylene cyanohydrin, heated to 300-350 degrees C in a glass or porcelain tube, gives 80-90% of acrylonitrile and methanol [58]. The ethyl ether of ethylene cyanohydrin, in contact with anhydrous orthophosphoric acid supported on pumice, gives 80-90% of acrylonitrile and ethanol at 360-400 degrees C [59].

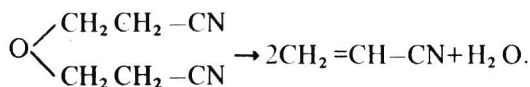
Clemo and Walton [60] prepared acrylonitrile by heating ethylene cyanohydrin *p*-toluenesulfonate with alkalis:



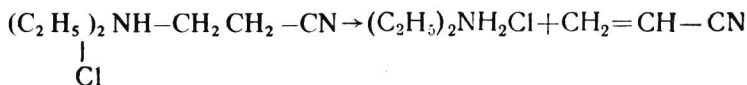
Acrylonitrile may be obtained by the pyrolysis of succinonitrile at 500-600 degrees C in the presence of an inert material [61]:



or by the pyrolysis of beta,beta-bis(2-cyanoethyl) ether [62, 63] at 400-500 degrees C in the presence of alkali metal salts of weak acids (potassium formate, potassium or sodium acetate, sodium phosphate, sodium tetraborate, etc.). The yield of acrylonitrile is 94%.



Acrylonitrile is formed in the decomposition of some amino derivatives of propionitrile. The dry distillation of the appropriate salt of beta-diethylaminopropionitrile produces acrylonitrile together with diethylamine hydrochloride [64]:



The reaction is carried out at 160-190 degrees C with a 77% yield of acrylonitrile.