Water-Soluble Polymers Technology and Applications 1972

Yale L. Meltzer

Water-Soluble Polymers

Technology and Applications

1972

Yale L. Meltzer

Thirty-Six Dollars

NOYES DATA CORPORATION

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FOREWORD

The detailed, descriptive information in this book is based on the U.S. patent literature since 1966 relating to the manufacture and use of water-soluble polymers.

The patents included in the chapter on starch, modified starch and derivatives are very recent, all issued since 1971, because there is such a large mass of material in this important and very active field.

For a detailed review of the earlier work in this particular field, the reader is referred to "Starches and Corn Syrups" by Dr. A. Lachmann, Noyes Data Corporation 1970.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legalistic phraseology, this book presents an advanced commercially oriented review of water-soluble polymers and the associated technology.

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".

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 utilizable 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.

These publications are bound in paper in order to close the time gap between "manuscript" and "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

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 easily obtainable information.

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INTRODUCTION

Synthetic water-soluble polymers are making increasing inroads into the more than 10,000 million pound per year worldwide water-soluble polymer market. These inroads have been made primarily in the industrialized countries of the world, especially in the United States, Japan, West Germany, the United Kingdom, France, the Netherlands and Italy. Adequate figures are not available on production in the Eastern European countries, the Soviet Union and Mainland China, but it is known that the Eastern European countries and the Soviet Union have substantial production facilities and that they are involved in further expansion of their output. Mainland China has a need for much of the required know-how.

One reason why the synthetics have been successful is that the use of traditional starch products in many industrial operations has been found to cause stream pollution, while the synthetics, with lower B.O.D. (Biological Oxygen Demand), have sharply reduced such pollution. In addition, the synthetics can be controlled more directly for end uses than the traditional starch products and the natural gums. As a result of the growth of the synthetics, starch manufacturers have improved their processing of starch and have concentrated research and development heavily upon developing modified starches and starch derivatives. The starches, modified starches and starch derivatives, in the competitive struggle for markets, have the great advantage of usually being much less expensive than the synthetics.

The vastly overwhelming portion of worldwide water-soluble polymer production consists of starch products (estimated at over 9,000 million pounds), followed in size by the natural gums, and the synthetics, polyvinyl alcohol and cellulose ethers. Smaller amounts are accounted for by the synthetics, acrylamide polymers, acrylic acid polymers, ethylene oxide polymers, polyethylenimine and polyvinylpyrrolidone.

Classifications: In the trade, water-soluble polymers are also known as "water-soluble resins," "hydrocolloids," and "gums."

Applications: Some of the main applications of water-soluble polymers are in adhesives, construction, cosmetics, detergents, explosives, food, oil-well drilling, paints, paper, pharmaceuticals and textiles. For individual countries and individual water-soluble polymers, the breakdowns often vary widely.

Rheology: One very basic characteristic of water-soluble polymers is the viscosity of solutions. There are several methods for measuring viscosity (e.g., use of the Hoeppler Viscosimeter, the Scott Viscosimeter and the Brabender Amylograph), but a particularly popular one is the determination of the shear stress of the solution against the rate of shear through the use of the Brookfield Synchro-Lectric Viscometer. The Brookfield Viscometer employs spindles which rotate in the solution at controlled speeds which can be varied. Viscosity is usually stated in units of centipoises.

The viscosity of aqueous solutions of water-soluble polymers is temperature-dependent, with the relationship exponential. Thus, a small change in temperature can result in a very large change in viscosity. Water-soluble polymer solutions are non-Newtonian (i.e., as the rate of shear increases, the shear stress does not increase in the same proportion), with few exceptions. Some non-Newtonian fluid properties are pseudoplasticity, plasticity and dilatancy. In addition, there are water-solube polymer solutions which are thixotropic. For certain applications, it is desirable to have thixotropic solutions, for example, in special paints.

Yale L. Meltzer January 31, 1972

MARKET SURVEY

STARCH

Corn starch accounts for over one-half of the approximately 9,000 million pounds of starch produced in the world (excluding Eastern Europe, the Soviet Union and Mainland China), potato starch for about 30% and wheat, rice, tapioca and sago starches comprise most of the remainder. For the period 1960 to 1964, the U.S. Department of Agriculture has determined that, on the average, more than 5,000 million pounds of starch were produced in the United States by wet milling. About 60% of output was converted to syrup, sugar, dextrin and other products, and the remainder was shipped as starch.

The prices of starches are subject to such factors as the uncertainties of crop production (e.g., weather conditions) and governmental policies. Thus, the 1971 bumper crops of corn and wheat in the United States resulted in low grain prices in the latter part of 1971. The actual 1972 price structure, however, will depend upon the policy of the U.S. Government.

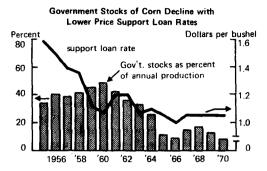
Grain Crop Price Structure

The last period of high price support loan rates by the U.S. Government (i.e., the rates at which farmers in the U.S. federal program may obtain nonrecourse government loans) was in the 1950's. During most of that decade, corn price support loans averaged over \$1.50 per bushel compared to an average of \$1.05 per bushel in recent years. Actual market prices of corn during most of the 1950's, averaged well above prices in recent years, but below the then existing support loan rates. For example, in the immediate post-Korean War period of 1953 to 1954, seasonal average corn prices received by U.S. farmers declined to \$1.46 per bushel compared to an average support loan rate of \$1.61 per bushel. Since enactment of the 1962 feed grain program, farm price support loan rates have been lower and closer to market clearing levels, with farmers receiving additional income support through direct payments. Between 1965 and 1970, corn prices averaged \$1.17 per bushel compared to an average loan rate of \$1.05 per bushel.

During 1971, with the blight- and drought-reduced 1970 corn corp resulting in high grain prices, U.S. farm policy moved closer to a market-orientated agricultural system following removal of feed grain and wheat acreage restrictions. The Federal Reserve Bank of Chicago has pointed out that under previous farm programs, planted acreage of feed grains and wheat was restricted to the farm's feed grain base and wheat allotment. Under the 1971 programs, cooperating farmers were allowed to plant as much of any crop as they wished regardless of their base or allotment after setting aside a specified amount of cropland. Farmers responded to the relaxed government controls and high market prices in the spring of 1971 with a sharp increase in feed grain and wheat acreage. The increased acreage coupled with very favorable growing conditions resulted in a record-large grain harvest and sharply lower prices.

The 1971 experience reaffirms the chronic tendency of farmers to overproduce in the absence of effective production controls and no program has yet solved this problem. High price support loan programs have resulted in large government—owned surplus stocks and eventual disposal problems. Direct payment and lower price support programs, on the other hand, have resulted in steadily rising payments to farmers to curb production.

During the 1950's, government stocks of corn (owned and under loan) rose from a Korean War low of 300 million bushels to 1,400 million bushels. By 1959, stocks were equal to over 40% of annual production. After the enactment of the 1962 feed grain program, government-controlled surplus stocks were gradually reduced. In 1970, they equaled 13% of annual production. Stocks dipped to 8% of production, following the blight- and drought-reduced crop of 1970. As government stocks declined, however, direct outlays to farmers increased sharply. Payments to feed grain producers increased from about \$840 million in 1962 to \$1,300 million in 1970 (or 55%). The graph shown on the following page indicates the trend of U.S. Government corn stocks for the period 1955 to 1970.



Source: Federal Reserve Bank of Chicago

The "Strategic Grain Reserve Bill" proposes stockpiling of feed grains and wheat and boosting government support loan rates for these commodities by 25%. A strategic stockpile of grain, while boosting support loan rates, probably would have the immediate effect of raising farm prices. As experience has shown, however, the higher prices would be short-lived unless direct government payments were increased to remove more cropland from production or government surplus stocks were allowed to build to absorb the increased production resulting from the higher prices. Either alternative would require a substantial increase in government outlays for agriculture, which comes at a time of a general U.S. federal policy of budgetary restrictions.

Com prices in early 1972 will depend largely upon the amount of direct government purchases and the extent to which farmers take advantage of the government loan program. Direct purchases of corn have so far been small, but corn placed under loan is running more than triple the year earlier level. Almost 85% of the U.S. crop is eligible for government loans in 1972, compared with only 44% in 1971.

Corn supplies exceed expected needs by 1,400 million bushels in the 1972 marketing year, the largest excess supply in seven years. As a result, corn prices will likely average near the support loan rate of \$1.08 per bushel plus storage and handling charges. A large increase in idled acreage this year, however, could provide strength to corn prices late in 1972. The announced goal of the U.S. Department of Agriculture is to idle 38 million feed grain acres in 1972, which is double that of 1971. If achieved, this is expected to result in a 12% reduction in corn acreage from 1971 (See Federal Reserve Bank of Chicago, Agricultural Letters of January 7, 1972.)

Corn Starch and Corn Syrup Price Structure

A sharp drop in the prices of corn starch and corn syrup took place in the fourth quarter of 1971 as a result of the enormous bumper corn crop that year. The entire price structure of the corn starch-corn syrup market became abnormally depressed and this condition has persisted into early 1972, with prices presently quoted at \$5 to \$5.15 per hundred pounds for unmodified corn starch. Prices are likely to move up until mid 1972, but as the year progresses U.S. governmental policy can be expected to make its effects more strongly felt. In October 1971, when the sharp drop in corn starch and corn syrup set in, CPC International, the world's largest private purchaser of corn, was instrumental in stabilizing prices. CPC International is also the world's largest corn refiner and manufacturer of starch, corn syrup, dextrose and corn oil.

Major U.S. Producers of Corn Starch

American Maize-Products Company
Anheuser-Busch, Incorporated
Clinton Corn Processing Company (a division of Standard Brands, Inc.)
CPC International, Incorporated
Hubinger Company
National Starch and Chemical Corporation
Penick & Ford, Ltd. (a subsidiary of R.J. Reynolds Industries)
A.E. Staley Manufacturing Company
Miles Laboratories, Incorporated

NATURAL GUMS

There are many types of natural gums. They are polysaccharides obtained from plants, trees and seeds. Production takes place in many parts of the world. Some well-known natural gums are listed below:

Guar Gum — Obtained from the seeds of plants grown in India, Pakistan and the United States.

It is used in ice cream, sherbets, cream cheese, oil-well drilling muds, paper and pharmaceuticals.

Gum Arabic (Gum Acacia) — An exudate from the bark of the acacia tree found in Senegal, the Sudan, Turkey and other countries. It is used in foods, beer and other beverages.

Gum Tragacanth — An exudate from the Asiatic plant Astragalus gummifer. It is used in dietetic foods, salad dressings, ice cream, candies and hand lotions.

Karaya Gum — Exudate of the Sterculia trees of India. It is used as a bulk laxative and dental adhesive, and in ice cream, paper and textiles.

Locust Bean Gum (Carob Bean Flower) — Obtained from the seed of the Mediterranean locust tree Ceratonia siliqua. It is used in cakes, ice cream, oil-well drilling muds, paper processing, textiles, and as an antidiarrheic.

These are only a few of the many natural gums. It is extremely difficult to determine how much natural gum is produced in the world because the occurrence of the plants, trees and seeds is so widespread and production and use of the gums often remains unknown.

Import Statistics

Below are U.S. import statistics for the natural gums enumerated above for the period 1964 to 1970:

TABLE 1: U.S. IMPORTS OF SOME NATURAL GUMS (1964 to 1970)

Year	Net Quantity (in pounds)	Net Value (in dollars)	
1964	68, 257, 377	14, 435, 403	
1965	83, 269, 897	15,706,795	
1966	87, 119, 243	16,993,385	
1967	77,554,965	16, 981, 410	
1968	64, 892, 349	15, 269, 858	
1969	68, 368, 947	18, 892, 623	
1970	73,618,163	21,853,085	

Note: The gums included are guar gum, gum arabic, gum tragacanth, karaya gum and locust bean gum.

Source: U.S. Bureau of the Census

In the following tables, statistical breakdowns are given on U.S. imports of some natural gums.

TABLE 2: U.S. IMPORTS OF GUAR GUM (1964 to 1970)

Year	Net Quantity (in pounds)	Net Value (in dollars)	
1964	26, 688, 456	4,069,813	
1965	38,066,938	4, 440, 739	
1966	36, 319, 617	4,621,382	
1967	21, 207, 421	2,840,059	
1968	15, 106, 888	2,098,034	
1969	20, 496, 384	3, 193, 425	
1970	26, 296, 750	4,538,595	

Source: U.S. Bureau of the Census

TABLE 3: U.S. IMPORTS OF GUM ARABIC (1964 to 1970)

Year	Net Quantity (in pounds)	Net Value (in dollars)	
1964	21,979,853	3,970,424	
1965	25,084,576	4,652,114	
1966	27, 854, 824	5, 392, 098	
1967	32, 268, 480	7,622,563	
1968	25,591,889	5,682,484	
1969	26,748,986	6,677,815	
1970	27, 080, 374	7,404,331	

Source: U.S. Bureau of the Census

TABLE 4: U.S. IMPORTS OF GUM TRAGACANTH (1964 to 1970)

Year	Net Quantity (in pounds)	Net Value (in dollars)	
1964	1,358,594	1,584,330	
1965	1,325,636	1,489,981	
1966	1,794,828	2,077,202	
1967	3,730,986	2, 191, 397	
1968	1,774,673	2,586,535	
1969	1,791,351	2,890,009	
1970	1,707,546	3, 201, 819	

Source: U.S. Bureau of the Census

TABLE 5: U.S. IMPORTS OF KARAYA GUM (1964 to 1970)

Year	Net Quantity (in pounds)	Net Value (in dollars)	
1964	7,682,267	2,544,675	
1965	9,061,322	3,024,289	
1966	7, 224, 384	2, 134, 664	
1967	7, 201, 505	1,646,267	
1968	7,344,074	1,748,378	
1969	6,774,342	2,496,880	
1970	7,645,736	3, 200, 263	

Source: U.S. Bureau of the Census

TABLE 6: U.S. IMPORTS OF LOCUST BEAN GUM (1964 to 1970)

Year	Net Quantity (in pounds)	Net Value (in dollars)	
1964	10,548,207	2, 266, 161	
1965	9,731,425	2,099,672	
1966	13, 925, 590	2,768,039	
1967	13, 146, 573	2, 681, 124	
1968	15,074,825	3, 154, 427	
1969	12,557,884	3,634,494	
1970	10,887,757	3,508,077	

Source: U.S. Bureau of the Census

POLYVINYL ALCOHOL (PVA)

Rapid growth of Jully hydrolyzed PVA for use in polyester-cotton blend warp sizing has caused the PVA market to sharply expand. In the United States especially, demand is consderably greater than the domestic supply for some PVA grades, causing customers, particularly textile manufacturers, to rely a great deal on imports. Competition in the PVA market is extremely intense, with the main competition coming from the Japanese producers. As a result, price weakness has plaqued this market over the past few years.

Applications

TABLE 7: BREAKDOWN BY APPLICATION IN THE UNITED STATES

Textile warp sizing	43%
Adhesives	25 %
Paper coating	15%
Miscellaneous	17%
Total	100%

Source: Chemical Marketing Reporter, April 1, 1970

Producers

TABLE 8: UNITED STATES PRODUCERS

	Capacity*
Air Products & Chemicals, Inc.	30
Borden, Inc.	8
DuPont	15
Monsanto	12
Total	65

^{*}Millions of pounds annually for PVA not used in manufacture of polyvinyl butyral.

Note: Air Products & Chemicals, Inc. acquired its capacity from Air Reduction (now Airco, Inc.) on January 28, 1971 when it purchased Air Reduction's Chemical and Plastics Division and paid for an 8-year lease on Air Reduction's

Calvert City, Kentucky facilities.

Source: Chemical Marketing Reporter, April 1, 1970 and company information.

An important U.S. Producer of PVA for which capacity figures are not available is CPC International, which markets a broad range of fully and partially hydrolyzed grades. Du Pont is building a new PVA plant at LaPorte, Texas, which is expected to be the world's largest PVA plant. It is scheduled to go on-stream in 1972 and should more effectively meet the strong thrust of Japanese competition than has been the case up till now. Japan presently possesses the world's largest capacity of PVA. The main Japanese producers are Denki Kagaku Kogyo K.K., Kuraray Co., Nippon Synthetic Chemical Industry, Shin-Etsu and Unitka Chemical Compnay. In West Germany, the main producer is Farbwerke Hoechst.

Price

Price weakness has characterized this market. In the United States, the current price (1972) is \$0.32 per pound delivered for fully hydrolyzed PVA. The high for the period 1957 to 1972 was \$0.67 per pound for fully hydrolyzed grades (bags, truckload, F.O.B. selling point); the low \$0.32 per pound delivered.

Growth and Forecasts

For the period 1960 to 1969, it is estimated that overall U.S. PVA consumption has grown at 8% per year. For the period 1969 to 1974, it is expected that consumption will grow at 25% per year. The textile warp size market is expected to provide most of the impetus for the sharp increase in growth. An estimated U.S. production of 1.4 billion pounds of polyester broadwoven goods in 1974 should require 105 million pounds of synthetic size (mostly PVA). The available figures for U.S. production and U.S. sales by original manufacturer are given below:

TABLE 9: U.S. PRODUCTION AND SALES OF PVA (DRY BASIS)

Year			Sales by Original Manufacturer			
	Production (in pounds)	Quantity (in pounds)	Value (in dollars)	Unit Value		
1966	38, 337, 000	37, 926, 000	16,438,000	\$0.43		
1967	43, 484, 000	37,008,000	16, 236, 000	0.44		
1968	45, 168, 000	39,083,000	16,555,000	0.42		
1969	57,003,000	50,702,000	17,308,000	0.34		

Note: Preliminary figures for 1970 show U.S. production at 49,037,000 pounds; sales and use at 39,307,000 pounds.

Source: U.S. Tariff Commission

TABLE 10: ESTIMATED U.S. PVA CONSUMPTION (DOMESTIC SALES PLUS IMPORTS)

<u>Year</u>	Quantity (in pounds)		
1969	68,000,000		
1970	73,000,000		
1974	200,000,000		

Source: Chemical Marketing Reporter, April 1, 1970

CELLULOSE ETHERS

There are many types of cellulose ethers produced and their manufacture is of worldwide scope, which includes many of the Communist-bloc countries (e.g., Czechoslovakia, East Germany, Hungary, Poland and the Soviet Union). Total worldwide production of cellulose ethers is estimated to presently come to 180 million pounds, with sodium carboxymethyl-cellulose (CMC) accounting for approximately 65% and the remainder consisting mainly of the methyl celluloses, ethyl celluloses, hydroxyethylcellulose (HEC) and hydroxypropylcellulose (HPC).

Basic Information

The main raw materials for cellulose are wood pulp and cotton linters. These are readily available, which makes the manufacture of cellulose ethers economically attractive. Cellulose itself is not soluble in water. It consists, however, of a polymeric chain of anhydroglucose units, with each anhydroglucose unit possessing three hydroxyl (OH) groups. The hydrogen atoms in the OH groups can, therefore, be replaced under the proper reaction conditions. Thus, when a base, such as aqueous sodium hydroxide, is added, it causes the cellulose molecule to swell. This serves to activate the hydroxyl groups on the cellulose anhydroglucose unit. Various etherification agents can then be added to yield cellulose ethers which are soluble in water.

There are varying degrees of substitution possible up to a maximum of 3. The degree of substitution (D.S.) is sometimes referred to as the degree of etherification. Most commercially available CMC grades fall in the range D.S. 0.4 to 1.2. In the case of HEC, however, in addition to the substitution of hydroxyethyl groups on the cellulose molecule itself, it is possible for the etherification agent ethylene oxide to react with the already substituted hydroxyl groups to form side chains. Therefore, the mols of substitution or molar substitution (M.S.) can be greater than 3. Commercial HEC, however, is usually in the M.S. range 1.8 to 2.5.

In addition to variations in D.S. or M.S. for the various cellulose ethers, there are variations in the degree of polymerization and purity, as well as other factors (e.g., the pH, the presence of salts and particle size), which yield a wide variety of commercially useful products.

Production and Sales of Cellulose Ethers

Below are given the available figures for total U.S. production and sales of all cellulose ethers:

TABLE 11: U.S. TOTAL PRODUCTION AND SALES OF CELLULOSE ETHERS

Year		Sales by Original Manufacturer		
	Production (in pounds)	Quantity (in pounds)	Value (in dollars)	Unit Value
1963	79,52 7 ,000	72,338,000	39,620,000	\$0.55
1964	85,805,000	79, 294, 000	43,521,000	0.55
1965	91,308,000	85,101,000	46,880,000	0.55
1966	95,933,000	90,523,000	50, 489, 000	0.56
1967	103, 916, 000	92,487,000	51,402,000	0.56
1968	117, 228, 000	106,025,000	58,047,000	0.55
1969	122,419,000	115,807,000	64,615,000	0.56

Source: U.S. Tariff Commission

SODIUM CARBOXYMETHYLCELLULOSE (CMC)

As a result of the movement towards low phosphate and nonphosphate detergents, the CMC market has recently improved. Prices 'ave firmed considerably compared to the stringent price competition of a few years ago, particularly in the detergent-grade market. Prospects for food-grade CMC look very promising and the food-grade market should grow at twice the anticipated 3% per year growth rate for the overall CMC market in the United States.

In the food area, particularly promising areas are in low-calorie foods and beverages, cake mixes, dehydrated foods, ice cream, pet foods and salad dressings. The paper size and textile warp size markets, however, have not shown growth nor do they look promising. Resistance from other water-soluble polymers in the paper size market has been extremely strong, while CMC has been meeting severe competition from PVA in the textile warp size market.

Applications

TABLE 12: BREAKDOWN BY APPLICATION IN THE UNITED STATES

Detergents	28%
Textiles	24%
Foods	20%
Oil-well drilling muds	10%
Paper sizing	5%
Miscellaneous	13%
Total	100%

Source: Chemical Marketing Reporter, November 1, 1971

U.S. Producers

It is estimated, by the Chemical Marketing Reporter, November 1, 1971, that of a total U.S. capacity of 71 million pounds per year of CMC, Hercules has the largest capacity at 40 million pounds per year, DuPont is second at 15 million pounds per year and Procter & Gamble's Buckeye Cellulose Corporation is third at 7 million pounds per year.

Price

In the United States, for the period 1952 to 1972, the high price was \$0.45 per pound (crude, low or medium viscosity, bags, 23,000 pounds, delivered East of the Rocky Mountains, 100% basis); the low price, \$0.37 per pound (same basis). The current price (1972) is \$0.45 per pound (same basis), with sales to detergent manufacturers at \$0.38 per pound (carlot, same basis).

Growth and Forecasts

For the period 1960 to 1970, growth of the overall U.S. CMC market (in terms of consumption) was 3.8% per year, with growth expected to fall to a 3% rate for the period 1970 to 1975. Some areas of the market, however, should grow above this rate. The large soap and detergent manufacturers (e.g., Procter & Gamble, Lever Bros. and Colgate-Palmolive) are looking for detergent systems that can meet the antipollution requirements which have been established by some municipalities and which are in the process of being formulated by others. CMC could benefit, but there has as yet been no strong movement in any one direction regarding such systems. Another market that holds promise for future growth is use of CMC as a soil-release agent in wash-and-wear garments. At this time, the food market shows the greatest tangible potential for growth. In the oil-well drilling mud market, CMC has been losing ground to the lignosulfonates and can be expected to continue to do so, unless some significant technological breakthrough takes place. Figures for U.S. production and U.S. sales by original manufacturer are given below for the period 1960 to 1969:

TABLE 13: U.S. PRODUCTION AND SALES OF CMC (100%)

Year	•	Sales by Original Manufacturer		
	Production (in pounds)	Quantity (in pounds)	Value (in dollars)	Unit Value
1960	42,660,000	38,310,000	17,711,000	\$0.46
1961	47,604,000	41,665,000	18, 984, 000	0.46
1962	43, 488, 000	41, 119, 000	18, 298, 000	0.44
1963	42,741,000	41,495,000	18, 532, 000	0.45
1964	44, 930, 000	42, 454, 000	18,712,000	0.44
1965	48,770,000	45, 242, 000	19,057,000	0.42
1966	48,736,000	48, 355, 000	20,758,000	0.43
1967	54,750,000	50,816,000	21, 290, 000	0.42
1968	59, 951, 000	58,605,000	24,750,000	0.42
1969	61,586,000	62,349,000	26, 254, 000	0.42

Source: U.S. Tariff Commission

TABLE 14: ESTIMATED U.S. CMC CONSUMPTION (DOMESTIC SALES PLUS IMPORTS)

<u>Year</u>	Production (in pounds)	
1970	62,000,000	
1971	. 64,000,000	
1975	72,000,000	

Source: Chemical Marketing Reporter, November 1, 1971

For further information on CMC, the reader is referred to the following articles by the author:

Yale L. Meltzer, Soap & Chemical Specialties (November 1968), pp. 72, 74 and 76.
Yale L. Meltzer, Soap & Chemical Specialties (December 1968), pp. 122, 124 and 135 to 136.

ACRYLIC ACID AND METHACRYLIC ACID POLYMERS

Applications of Polyacrylic Acids and Their Salts

Adhesives
Binders
Coatings
Desalinization
Dispersants
Emulsion paints
Films
Laminated structures
Thickeners
Water treatment

Producers

TABLE 15: MAJOR U.S. PRODUCERS

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Alco Chemical Corporation American Aniline & Extract Company Diamond Shamrock B.F. Goodrich

W.R. Grace & Company

Jordan Chemical Company Rohm and Haas Company

Products

Sodium polyacrylate
Polyacrylic acids
Polyacrylic acids and sodium polyacrylate
Ammonium polyacrylate and sodium polyacrylate
Sodium salt of polymethacrylic acid and sodium polyacrylate
Sodium polyacrylate
Sodium polyacrylate

Acrylic emulsion copolymers, polyacrylic acids and sodium polyacrylate

Source: U.S. Tariff Commission

Polyacrylic Acid Salts

TABLE 16: U.S. PRODUCTION AND SALES OF POLYACRYLIC ACID SALTS

Year		Sales by Original Manufacturer		
	Production (in pounds)	Quantity (in pounds)	Value (in dollars)	Unit Value
1960	1,818,000	1,766,000	1,949,000	\$1.10
1961	1,457,000	1,205,000	1,569,000	1.30
1962	1,492,000	1, 232, 000	1,705,000	1.38
1963	2,577,000	2,501,000	2,818,000	1.13
1964	N.A.	N.A.	N.A.	N.A.
1965	2,492,000	3,326,000	4,030,000	1.21
1966	2,806,000	3,527,000	4, 147, 000	1.18
1967	2,379,000	3,324,000	3,851,000	1.16
1968	5,206,000	4, 875, 000	5, 452, 000	1.12
1969	4,213,000	4,470,000	5,131,000	1.14

Source: U.S. Tariff Commission

N.A. = Not Available

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