

Handbook of Water-Soluble Gums and Resins

ROBERT L. DAVIDSON

Editor in Chief

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McGRAW-HILL BOOK COMPANY

New York St. Louis San Francisco Auckland Bogotá
Hamburg Johannesburg London Madrid Mexico
Montreal New Delhi Panama Paris São Paulo
Singapore Sydney Tokyo Toronto

Main entry under title:

Includes index.

1. Gums and resins—Handbooks, manuals, etc.*

I. Davidson, Robert L.

TP978.H26

668'.37'0202

79-24007

ISBN 0-07-015471-6

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1234567890 KPKP 89876543210

The editors for this book were Harold B. Crawford and Joseph Williams, and the production supervisor was Thomas G. Kowalczyk. It was set in Gael by The Kingsport Press.

Printed and bound by The Kingsport Press.

Preface

One cannot do justice in a few words to the omnipresence of water-soluble gums and resins. It is virtually impossible for a day to pass without each of us having benefitted from one of these materials, either in the clothing we wear, the foods we eat, the beverages we drink, the toiletries or cosmetics we use, the medicines we take, and more. Much more. A scan of the index will convert the most obdurate of skeptics.

This book is designed to be used. Both organization and writing are tailored for speedy, accurate referencing. Each chapter is divided by category and subcategory with a degree of built-in redundancy so that users can enter it according to their different needs, for example:

- by gum or resin
- by basic function
- by end product
- by industry
- by property or characteristic

The text is supported by a detailed index. With it, one can locate both major and minor uses, applications, interactions, compatibilities, system components, or whatever other data is required. Together, these data-search aids implement the editor's conviction that the utility of a reference work, regardless of its content, is no better than the speed and accuracy with which a user can enter and search the work.

The cumulative qualifications of the authors is gratifying. Their biographies and, where available, photographs are presented in the "Editorial Advisors and Contributors" section, beginning on page ix. In particular, I owe much to John Glavis, formerly of Rohm and Haas,

and now deceased; Kenneth Guiseley of FMC's Marine Colloids; Morton Rutenberg of National Starch and Chemical; and George Greminger of Dow Chemical. Their generous consultation and expert advice was invaluable in the planning of the book.

One final note, a caveat. The information in this book is offered solely for your consideration. It is not a warranty or recommendation for the use of any product, nor for the practice of any procedure or patented invention without prior investigation and verification of your own.

Robert L. Davidson
Editor in Chief

Editorial Advisors and Contributors

EDITORIAL ADVISORS

FRANK JOHNSON GLAVIS

Research Chemist, Rohm and Haas Company, Philadelphia, Pennsylvania, from 1938 to 1974; retired 1974; deceased June 11, 1976. He received his A.B. degree from Dartmouth College in 1935, and his Ph.D. degree from the University of Illinois in 1938, when he joined Rohm and Haas. He was the author of twenty-five U.S. patents, and the holder of many foreign patents in the fields of synthetic lubricants, additives for lubricants, and monomer preparation, as well as for the polymerization and use of acrylic and methacrylic acids and their derivatives, especially the esters. Among his many contributions to polymer science, he developed a method for the hydrolysis of methacrylic polymers, used as a chemical means of distinguishing the isotactic and syndiotactic forms of such polymers.

Dr. Glavis was a man of indomitable will who, despite diabetes since the age of 10 and blindness since the age of 35, continued a fruitful scientific career in chemistry. His interests were broad ranging, and included not only polymer chemistry, but ice skating, sailing and boating, music, and reading. He was a family man, married in 1940 to Doris Ashworth who, with their daughter, Wendy Jane, survives. His courage will be remembered, his kindness will be missed.

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Associate Director, Starch Modification Research, Starch Division, National Starch and Chemical Corporation, Bridgewater, New Jersey; received his B.S. degree (1942) and M.S. degree (1947) in chemistry, and his Ph.D. degree (1949) in organic chemistry from the University of Pennsylvania. He joined National Starch as Chemist in 1949, advancing through Supervisor, Protein Research, and Section Leader in By-Products Research to his present position in 1973. He has worked in starch chemistry and technology, polysaccharides, hemicelluloses, and natural gums. He is co-inventor on 19 patents on starch and hemicelluloses. He is a member of the American Chemical Society, the American Association of Cereal Chemists, Sigma Xi, and the AAAS.



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Patent Agent, Patent Department, Rohm and Haas Company, Philadelphia, Pennsylvania; received his B.S. degree in chemistry from Pennsylvania State College in 1939, and his Ph.D. degree in chemistry from Columbia University in 1952. He became a registered patent agent (United States) in 1975. From 1941 to 1945, he was engaged in rocket propellant research for Division 8 of the National Defense Research Committee. He joined Rohm and Haas in 1950, and has worked on rocket propellants, surface chemistry, organic coatings, and aqueous polymer dispersions. His work has ranged from process development in oil recovery and emulsion polymerization to the physical properties of surfactants and polymer dispersions. He has contributed a number of scientific papers, patents, and book chapters in the above-named fields.



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**NORMAN F. STANLEY****Carrageenans**

Senior Scientist, FMC Corporation, Marine Colloids Division; largely self-educated in chemistry and mathematics. He began his career in seaweed hydrocolloids in 1940 as a laboratory technician with the Algin Corporation of America, and was promoted to Laboratory Manager in 1941, then to Research Director in 1953. From 1959 to 1964, he was Assistant Technical Director for Marine Colloids, and in 1964 he became Senior Chemist, receiving his present appointment in 1974. He developed processes to extract and modify carrageenan, holds a patent, has authored or coauthored seven publications on carrageenan chemistry, and is a member of the Society of Rheology, the American Chemical Society, the AAAS, and the AIChE.

**KENNETH R. STAUFFER****Gum Tragacanth**

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HENRY VOLK
Polyacrylamides

Research Specialist, Dow Chemical Company, Midland, Michigan. He joined Dow in 1943, and has been active in the research and development of water-soluble polymers for many years. His interests have included the synthesis and product development of polymers. He is the author or coauthor of seventeen patents, the majority of which are related to the preparation and/or utility of water-soluble polymers. He has also been involved with monomers synthesis; e.g., styrene sulfonic acid, tertiary butyl styrene sulfonic acid. His work on the flocculation properties of water-soluble polymers has led to an increased knowledge of the proper techniques for maximizing polymer performance.



PHILIP A. WHITEHOUSE, JR.
Carrageenans

Received his B.Sc. degree in chemistry from the University of Maine in 1962. For the next five years, he researched antineoplastic agents and natural products, coauthoring many papers on these subjects with Dr. G. R. Pettit. He joined Marine Colloids Division of FMC Corporation in 1967, and for 10 years was closely involved in all phases of carrageenan manufacture and applications, holding titles from Research Chemist to Assistant Production Manager. He established a system linking the finished application through the manufacturing process to the raw material. He coauthored one patent relating to the sulfation of polysaccharides and is a member of the Sigma Xi. He left Marine Colloids in 1977 to pursue an independent career in marketing.



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Polyvinylpyrrolidone

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Chapter 1

Introduction

D. F. Durso

Johnson & Johnson

Not many years ago, a comprehensive report on water-soluble gums and resins would have treated mainly natural materials. The few synthetic compounds were based on cellulose. With the advent of practical synthetic organic polymer chemistry, a revolution took place which greatly increased the variety of chemical compounds and physical reactions available. Users could almost specify independently each of the solution attributes they wished to obtain and confidently expect to purchase some stock or custom-made molecule to suit their needs. More recently, we are seeing another revolution in this field of "water modifiers." Today, the chemist is producing superabsorbents which differ from the past materials in that they do not dissolve but merely make the water part of their internal structure.

The most descriptive single term for all of these materials is *hydrogels*. These are substances which associate with water molecules in such a way that the behavior of the water is modified, allowing us to perform functions not normally possible. This change in water behavior is usually accomplished by minor amounts of the hydrogel, commonly less than 10% of the weight of the water.

There are many ways in which one could choose to group the water-soluble gums and resins so that the user of the Handbook might quickly acquire the desired information. After much deliberation and several false starts, the reader will find a combined chronological-source format which introduces this complicated but exciting and dynamic field. It should be noted that many "old" materials compete successfully today after almost a century of efforts to replace them. Thus, it is the usual balance of economics and performance which determines the commercial realities.

Exudates

Originally the term *gum* was applied to the exudates from various plants. These substances were usually sticky and deformable masses produced in response to some injury. Centuries ago it was learned that these substances could be dissolved in water and then used in special ways. Perhaps lubrication and gluing would represent the extremes of the actions available. From some obscure beginning, procedures evolved for stimulating the production of gum by the plant, for purification of the raw material, for reduction to a shippable form, and for use in end products.

Despite the evolutionary indications in this report, it should be noted that a large

commerce exists today in many of the gums known even in ancient times. For many of them, the basic processes for their production and collection are unchanged from those used centuries ago. It is a testimony to the synthesis ability of plants that, in many cases, the natural exudates provide functions which cannot be equaled economically by man.

As will be seen in more detail later in this Handbook, the plant exudates are polysaccharides containing various sugars other than glucose, and having significant quantities of oxidized groups as an adjunct to their normal polyhydroxy format. In all cases, a large proportion of the groups are carboxyl, and these are found as salts of calcium, magnesium, or potassium rather than in the free form.

Extractives

In many cases, water-soluble polysaccharides in general similar to the exudates are components of land and marine plants and their seeds. These materials result from normal metabolic and life processes, and many times they represent the reserve carbohydrate in that system. In the latter case, the commercial value of the extract is such that the plant is cultivated for the express purpose of providing the gum. Unlike the rudimentary systems for collection and processing of the exudates, the extractive-type gums result from quite sophisticated ventures, including seed selection, plant placement, seed collection, and seed processing. In many cases, it will be seen that seed processing requires fractionation to obtain the desired commercial gum quality.

This class of gums includes those obtained from seaweeds and from trees. Here the entire plant is harvested and comminuted to increase accessibility; then the gum is removed by water leaching. The entire cost of the operations, including planting, can be borne by the gum product because of the inimitable properties of the natural material.

Like the exudates, these materials are salts of acidic polysaccharides. The polymer structures may be more varied and more complex than those of the previous group.

Synthetic, Natural-Based

Using purified cellulose as a starting material, organic chemists have learned to imitate or replace nature in many applications. The chief commercially important materials are those known as ethers, wherein the hydroxyl groups have been derivatized by a reaction which replaces the hydrogen atom with a simple or complex group.

The first and still largest-volume material is carboxymethylcellulose (CMC), made by the addition of chloroacetic acid to soda cellulose. In many cases, this material replaced the natural gums when problems arose because of economic, supply, or chaotic conditions. Originally needed to replace a long-standing natural material, this first synthetic gum developed a technology of use and production which has stood the test of time. Production of CMC has been increasing almost continually since its first commercial use and, like the natural gums, it has carved certain niches which cannot be filled by other similar hydrogels.

Unlike nature, man is not restricted to the use of carboxylic salt groups in order to accomplish the purpose of modification of water. Neutral (non-ionic) and basic groups can also be introduced. In some cases, the materials can pass through a water-soluble stage and become soluble in organic solvents. In other cases, the derivative group will impart water and solvent miscibility simultaneously. The possibilities here are limited only by the imagination of the chemist and the ability of the user to pay for the transformation of insoluble cellulose into a new form.

Among the present commercially important materials are these neutral ethers of cellulose: methyl-, ethyl-, hydroxyethyl-, and hydroxypropyl-. Details concerning their preparation and applications will be found elsewhere in this Handbook.

While starch can also be converted into almost all the same derivatives as cellulose, commercially there are no important neutral ethers. In many cases, starch itself serves as a hydrogel after enough processing to disrupt the natural structure of the starch granule. Huge amounts of corn and potatoes are processed each year in order to fill the needs of the industrial, technical applications where other "gums" cannot compete. It is quite literally true that the cellulose industry as we know it today, where the cellulose is used in solid form for its physical attributes, could not exist without the almost equal-volume industry which supplies starch in many grades.

Besides the uses for "natural" starch, there are many applications where the starch

has been made cationic by the incorporation of nitrogen-based groups. Here again, the hydroxyl hydrogen has been chemically removed and replaced by a substituent which provides a different "gum" reaction.

It has been known for many years that derivatives of cellulose and starch can be prepared by grafting. In these reactions, free radicals are generated within the substrate by some suitable catalyst system. Usually the hydrogen of the hydroxyl is eliminated and thus the oxygen atom serves as the site of the free radical. In the presence of suitable vinyl-type monomers, these active species will then cause a closely associated synthetic chain molecule to be produced. Whether the new molecule is attached covalently or by weaker bonds, the result is a major modification of the water-solubility of the natural substrate. The components of the final product can be further modified by chemical reactions generally known as "crosslinking." These can be as simple as internal ester formation (between hydroxyl and carboxyl groups), or they can be as complicated as those obtained by chemical additions to double bonds.

It should be obvious that with these tools available, a very large number of water-interacting "gums and resins" can now be prepared. In 1976, laboratory and commercial quantities of several materials were introduced into products where minimal water-solubility of the hydrogel is desired. The performance value of these new materials is yet to be proven, since they command a premium price over all previous "derivatives." Strangely, all of the current products are based on carboxylic ethers of cellulose or starch.

A relatively new group of cellulose-based gums are those containing sulfonic acid groups. These are being utilized where shortages of seaweed gums have provided the necessary economic basis.

Another large group of uses has arisen in recent years for gums produced by the action of fungi or bacteria (specifically, their enzymes) on natural materials, usually starch. These biologically produced polymers result from the almost total decomposition of the substrate into its monosaccharides followed by re-synthesis into new molecules utilizing some or all of these changes: points of attachment other than C₄, partial oxidation of the hydroxyl groups, interchain crosslinking, or introduction of new chemical groups to replace the hydroxyl hydrogen.

Synthetic

In this group are those hydrogel materials prepared from simple molecules, usually petroleum-based. In general, these are based on polymerization of vinyl-type monomers, and usually the monomer has been modified such that it contains an acidic (or acid-based) function. The materials were first synthesized as part of fundamental research projects, then tested for the possibility of replacing some of the gums mentioned previously, and finally accepted into some commercial uses because of unique properties.

Here again it is strange to note that with the myriad chemical moieties available to the organic chemist, the materials of interest contain hydroxyl and carboxyl groups, just like the "original" gums and resins.

These totally synthetic products have found applications in those fields where resistance to normal biological decomposition is needed. They can be structured so as to be impervious to the organisms (and their "natural" enzymes) requiring monosaccharide-based polymers. In addition, these products also can be prepared so as to permit usage at elevated temperatures where all other types discussed previously would decompose and/or lose their ability to interact with water molecules.

Summary

Depending on source, four major groups of water-soluble gums and resins have been identified. When examined chemically, we find that they are polymers with acidic, neutral, or basic groups scattered among the linear, branched, or crosslinked chain molecules. The materials are all used for the simple reason that, in rather minute amounts, they so alter the normal properties of water as to result in a valuable function. This can be in nutrition, in medicine, in graphic arts, in boxboard manufacture, etc.

The varied needs are such that a rather unbelievably large family of materials is available, and many of these are the basis for multimillion-pound annual commercial enterprises. Many of the suppliers can provide more than one material, and where required, they also provide applied technology in the form of special formulations prepared by them or instructions as to how the users can prepare their own custom gums.