

BOOK REVIEWS

N. G. GAYLORD, Editor

Catalysis. Volume 6. Hydrocarbon Catalysis.
PAUL H. EMMETT, Ed. Reinhold, New York,
1958. 640 pp. \$19.50.

A fundamental approach to the principles and practice of catalysis distinguishes Professor Emmett's renowned series of books on this subject. Volume 6 is a fitting addition to the series. In six chapters, it continues the fundamental approach of the earlier volumes while extending catalysis to the practical processes of petroleum chemistry.

The theory and practice of catalysis applied to hydrocarbon reactions is the major subject. The acid-catalyzed or carbonium-ion reactions are emphasized: alkylation, isomerization, polymerization to liquids, and cracking. Included also are an excellent chapter on catalytic reforming and a unique chapter on the mechanisms of polymer formation and decomposition.

The chapter on catalytic reforming is a thorough review of the catalysts and processes now in use and includes some previously unpublished material. Catalytic reforming introduces the dual-function catalyst in which hydrogenation-dehydrogenation properties control electronic processes and acidic centers control ionic processes. Because dual-function catalysts are not fully understood, this chapter contains less theoretical and mathematical information than the rest of the book. Dual-function catalysts that produce high-density polyethylenes and stereoregular polymers of higher olefins are as little understood as those used in reforming.

Of special interest to the polymer chemist is the chapter, "Mechanisms of Polymer Formation and Decomposition," by R. Simha and Leo A. Wall. It emphasizes the initiation reaction for polymerization and decomposition. The entire theory of polymerization and initiation is mathematically developed. For such an undertaking, Professor Emmett could not have chosen better authors.

Free-radical polymerization constitutes the largest share of the subject matter. The mathematical treatment of polymerization kinetics—including the measurement of absolute rate constants and control of degree of polymerization—is unusually complete. Specific cases are worked out for photo and thermal initiation, for peroxide initiation, and for promoted peroxide decomposition as related to inhibitor and retarder action. Initiation in redox and emulsion systems, initiation by electronic and biological means, and an excellent review of initiation by atomic radiation are included. The theory of measurement of absolute rate constants by rotating sector techniques is developed in greater detail than has appeared in any other text. A short section discusses polymerization with preformed polymer and includes polymer-induced polymerization and formation of graft and block polymers.

A section on cationic polymerization thoroughly reviews the catalysts and cocatalysts involved. Important cationic polymerization mechanisms are described, including the carbonium-ion mechanism and the effect of the counter-

ion. The treatment is less mathematical than that of free-radical initiation because the theory of cationic polymerization has not advanced as far.

The section on anionic polymerization reviews those cases in which involvement of anions is generally recognized; for example, when alkali metals and amides initiate polymerization and when lithium aluminum hydride, aluminum hydride, or aluminum alkyl is used as catalytic initiator. Preparation of crystallizable polymers is arbitrarily included as anionic polymerization. The material on preparing crystallizable polymers with dual-function solid catalysts is sketchy. Apparently the material was written early in the development of the field, judging from the references quoted. Many of the important technical developments as well as information relating to polymerization mechanism were passed over despite recent references added in an attempt to bring the subject up to date. This section does not measure up to the high caliber of the rest of the chapter. It reflects the authors' unfamiliarity with details in this facet of polymerization chemistry.

The remainder of the chapter concerns polymer degradation, which is the authors' major field. The theory of most features of depolymerization and degradation is thoroughly explained. Thermal, atomic, and oxidative degradation are described in both experimental and mathematical terms.

To the polymer chemist interested in a variety of initiation processes and in the problems of polymer stability, the chapter by Simha and Wall will make this book of great value. The rest of the volume on application of catalysis to petroleum processes serves as an extra bonus because of its high quality.

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Emulsions—Theory and Practice. (A.C.S. Monograph No. 135). PAUL BECHER. Reinhold, New York, 1957. ix + 382 pp. \$12.50.

The volume of published work in this field is so great that the author's decision to cite only significant early work, to tie in with developments in the past 15 years, and to limit patent references to those properly considered a part of the literature on emulsions, has resulted in a well-balanced presentation.

Necessary to an understanding of the technology is a background on surface activity, and this chapter provides a concise presentation of the theory involved. Because the interfacial film and its physical chemistry plays such an important part in emulsion formation and stability, this discussion has been quite complete.

The chapters lead logically from Physical Properties, through the theory of Emulsion Stability, Creaming, Inversion, and Demulsification. The selections of references to illustrate these phases of the subject were the outstanding contributions to this literature, and were knowledgeably handled. The chemistry of emulsifying agents includes a discussion based on the Schwartz and Perry classification and considers emulsifier efficiency and pertinent experimental data on this important phase of application.

Important to the experimenter is the chapter on Techniques: Good coverage of procedures and equipment is apparent. Current Applications are well authenticated and are either described by formulas and suggested method of preparation, or by wise selection of literature references. Though well presented, this chapter could have been expanded considerably, for this is the practice of the art about which so much has been written. A chapter on Demulsification in practice provides a short summary of the various applications in this specialty portion of the field.

Carefully prepared appendices round out the treatment of the subject: Appendix A, Testing of Emulsion Properties, devotes considerable space to surface and interfacial tension measurement; includes methods for measurement of viscosity, surface, and interfacial viscosity; determination of emulsion type; droplet size; stability; and several miscellaneous measurements. Appendix B, Commercially Available Emulsifying Agents, is a knowledgeable selection from the hundreds of surfactants on the market.

This book is recommended as a well-designed tool for one interested in theory, can be very useful from the application viewpoint, and has been planned for ease of usage.

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Rubber, Fundamentals of Its Science and Technology. J. LE BRAS, translated by IRENE E. BERCK. Chemical Publishing Co., New York, 1958. 464 pp. \$12.00.

This book is based on a course of lectures first given in 1941 by Professor Le Bras at the French Rubber Institute for the purpose of training rubber engineers and technicians in the research department of the institute. The subject matter has been revised and modernized since that time. The chapter titles are: General Aspects; Sources and Preparation of Natural Rubber; The Composition and Properties of Latex;

The Physical Properties of Rubber; The Chemical Composition and Structure of Rubber; The Chemical Properties of Rubber; Vulcanization; Compounding Ingredients and Their Application; Processing of Rubber; Direct Application of Latex; Theoretical Aspects of Rubber Chemistry; Synthetic Rubbers; Analyses and Tests for Latex and Rubber; Hard Rubbers, Reclaimed Rubbers, and Chemical Rubber Derivatives; Applications of Rubber.

As might be expected, the emphasis of the book is strongly on the practical. The properties of natural rubber and its processing, vulcanization, and testing are discussed with an ease and authority which bespeaks the author's long experience with these aspects of rubber science. The treatment of synthetic rubbers, while brief, is very useful and an effort has evidently been made to make it as up to date as possible. The discussion is very simple, for the most part, so that readers with only an elementary knowledge of chemistry should be able to follow it without difficulty. Readers of greater scientific sophistication will still find much that is helpful and valuable in the more technological sections of the book.

Unfortunately, in its more theoretical phases the book is considerably less successful. To do the author justice, it must be said that this phase of the subject was deliberately de-emphasized. Nevertheless, there are omissions which are difficult to understand. For example, there are only two very brief references to the use of infrared in the elucidation of rubber structure (the index lists only one reference), and no discussion or illustration of this important technique. Again, the reader interested in the molecular weight of rubber will find no mention of the light-scattering method for its determination, and will be led to believe that he must ordinarily rely on viscometry (no reference given later than 1926) or osmotic pressure. There is no discussion of molecular weight distributions and averages. A particular effort is made to treat the theory of vulcanization of rubber in some detail, because of its obvious importance, but the discussion is disappointing. Considerable space is given to outmoded theories, a tendency noticeable elsewhere in the book, while Farmer's work, which forms the basis of our modern understanding (such as it is) of sulfur vulcanization, is dismissed in three lines.

This book can be recommended to those who wish to know something of the technology of rubber, and either know already or are willing to neglect the more fundamental aspects of the field. It is well printed and relatively free from typographical errors, but is rather unattractively bound.

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