

however, sugar ferments so fast that the oxidation of lactic acid, the product of fermentation, does not keep pace with its formation. Result: Lactic acid builds up in the tumor, then spills over into the blood stream. Dr. Racker, R. Wu, and J. B. Alpers used a systematic analysis of the enzymes, cofactors, and regulatory mechanisms that take part in sugar metabolism to find the reason for the rapid production of lactic acid in tumors.

Oxidation of food takes place in specific intracellular structures called mitochondria. Glycolysis (fermentation of sugar) is catalyzed outside the mitochondria by soluble glycolytic enzymes. Oxidation as well as glycolysis needs certain cofactors such as nucleotide adenosine diphosphate and inorganic phosphate for proper function. Dr. Racker and his coworkers find that mitochondria and glycolytic enzymes compete for these cofactors. In normal cells, the oxidation process prevails; the glycolytic process is inhibited. In cancer cells, the enzyme which utilizes inorganic phosphate and the two enzymes which utilize adenosine diphosphate are present in such excess that they permit fermentation to proceed too rapidly.

Plastics' Aim— New Uses in Rockets

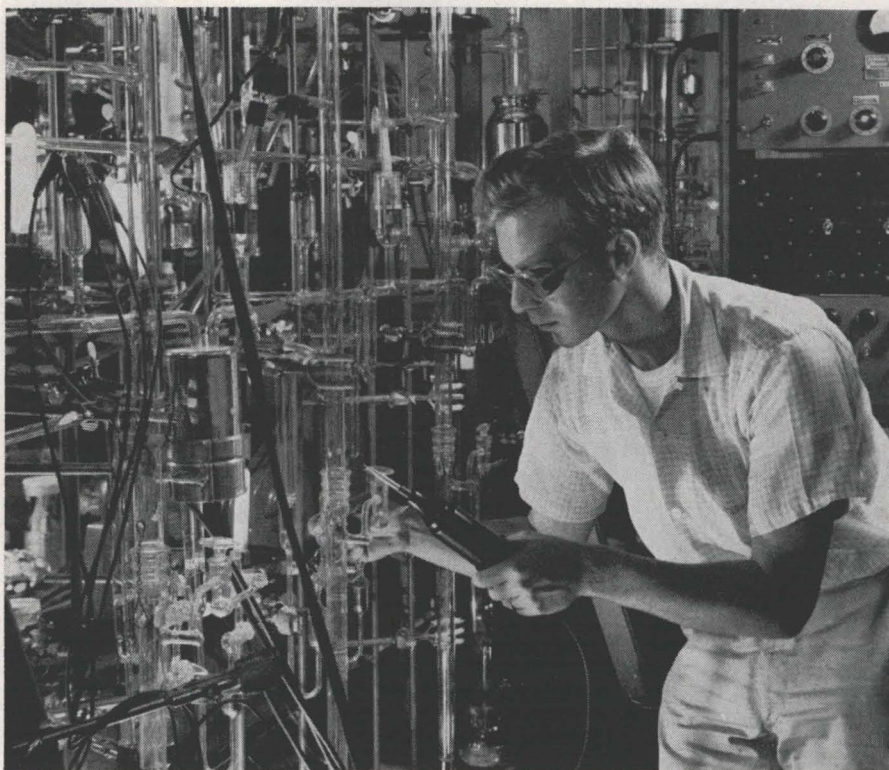
Aerojet studies plastic nozzles; ARC works on new plastic heat insulators

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Paint, Plastics, and Printing Ink Chemistry

Rocket engineers are taking an extra hard look at plastics these days. Atlantic Research Corp., for example, sees plastics, combined with ceramic or refractory materials, as promising heat insulators in rocket motors. And Aerojet-General Corp. has high hopes for plastic rocket motor nozzles.

ARC is out to find a better insulating flame shield than the carbon char formed by pyrolysis of plastics. Carbon char formed by current plastic insulators in rocket motors does much to prevent the insulation from eroding from the motor wall. But it can't hold up under the extended burning times



▲ Moly "Ideal" for Liquid State Studies

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Colloid Chemistry

Molybdenum disulfide, used as a dry lubricant where graphite won't work, gives an "ideal surface for studying fundamentals of the liquid state," says General Electric's Dr. Peter Cannon. MoS₂, says Dr. Cannon (shown checking a gravimetric adsorption system used in his experiments), has a lamellar structure which allows detailed study of interactions of relatively small numbers of gaseous atoms or molecules. These studies lead to an atomic theory of the liquid state, Dr. Cannon feels. One finding so far: The melting point of MoS₂ is at least 2375° C., not 1185° C., as published in the literature.

and ultrahigh temperatures reached by the newer rocket motors, ARC's Dr. Walter C. Hourt told the Division of Paint, Plastics, and Printing Ink Chemistry.

The firm is now studying combinations of high and low char-forming plastics with ceramics and refractories such as metal oxides, nitrides, carbides, zirconates, and titanates. Two approaches have been tried: using ceramic or refractory as the continuous phase, and adding them as a discontinuous phase in a continuous plastic matrix.

Each combination, says Dr. Hourt, has given an insulation superior in one or more properties to current rocket motor insulations. For example, evaluation of such composites in an oxyacetylene flame shows them to have much better erosion and thermal re-

sistance than carbon char, he claims.

Aerojet is working hard on a plastic rocket motor nozzle which will weigh less than current models and still be dimensionally stable under the necessary service conditions. Heat-resistant phenolic and phenolic-silicone resins currently appear to be most suited to such nozzles, Aerojet's George Epstein says. For reinforcement, glass fabric made of Refrasil (96 to 99% SiO₂) fiber gives the best performance, he believes.

Other conclusions reached by Aerojet: Fibrous fillers are better than non-fibrous fillers; for a given nozzle material and design, ablation rate depends on time, gas pressure, and stagnation temperature; and reinforcements oriented to provide an edge-grain effect (fibers lie perpendicular to gas flow) are desirable.

Two More Metallocenes Are Aromatic

Compounds of osmium and ruthenium with cyclopentadiene have aromatic character

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Inorganic Chemistry

Two additional organometallic compounds are now known to exhibit the rather unusual aromatic reactivity characteristic of ferrocene. Since the discovery of ferrocene [dicyclopentadienyliron(II)] in 1951, researchers have repeatedly confirmed that it possesses an aromatic system. Yet cyclopentadiene, from which it is derived, is completely nonaromatic.

Dr. Marvin D. Rausch, a National Science Foundation fellow working with Dr. Ernst O. Fischer and Dr. Heinrich Greibert at University of Munich, has shown that ruthenocene [dicyclopentadienylruthenium(II)] and osmocene [dicyclopentadienylosmium(II)] also undergo substitution reactions that are characteristically aromatic. And they have prepared for the first time some novel mixed ketones based on these compounds.

Dr. Rausch told the Committee on Organometallic Chemistry of the Division of Inorganic Chemistry that he and his fellow workers prepared ruthenocene and osmocene by reacting ruthenium trichloride and osmium tetrachloride with cyclopentadienylsodium. These two metallocenes react with acyl chlorides in the presence of aluminum chloride in a manner typical of aromatic Friedel-Crafts reactions. Both compounds can also be metalated with *n*-butyllithium to give (after carbonation and hydrolysis) mono- and dicarboxylic acids.

Thus ruthenocene and osmocene are aromatic in the same way as is ferrocene. The reactivity in Friedel-Crafts reactions decreases in the order, ferrocene, ruthenocene, osmocene. This, together with evidence from infrared and acid dissociation constant measurements, indicates that the ring-to-metal

bond becomes tighter as the molecular weight of the metal increases.

Finally, the fact that all of these metallocenes take part in Friedel-Crafts reactions makes it possible to prepare novel compounds containing two different metals. Ferrocenoyl chloride reacts easily with ruthenocene in the presence of aluminum chloride, for example, to give ferrocenyl ruthenocenyl ketone.

Cellulose Exchangers Get New Look

Cross linking cellulose before or during modification gives higher exchange capacities

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Cellulose Chemistry

Dr. John D. Guthrie and Austin L. Bullock, Southern Regional Research Lab., New Orleans, La., have developed a new method for upgrading ion exchange celluloses. Their method: Cross link the cellulose before or during chemical modification. This permits higher ion exchange capacities, yet maintains properties suitable for chromatography, the researchers told the Division of Cellulose Chemistry.

One of the big limitations of most cellulose ion exchangers is low capacity in comparison with ion exchange resins. However, the cellulose exchangers do have certain advantages over the resins. For one thing, they are much finer than ordinary resins and present a larger surface. Also, their open, porous structure permits the entrance or attachment of large molecules which aren't readily adsorbed by the resins.

Cellulose ion exchangers—as fabric, yarn, fiber, pulp, or paper—are now used extensively to fractionate and purify proteins, enzymes, nucleic acids, hormones, viruses, peptides, and amino acids.

► **More Capacity.** Cross linking prior to or during chemical modification, the USDA researchers found, increases exchange capacity of aminoethyl cellulose, carboxymethylated cellulose, and phosphonomethylated cellulose without excessive fiber swelling or solubility. Three examples:

- Total capacity of aminoethyl cellulose, for example, was increased from 0.7 to 1.8 milliequivalents per gram by cross linking with di(2-sulfatoethyl) amine prior to aminizing three times with 2-aminoethylsulfuric acid in the presence of sodium hydroxide.

- Total capacity of carboxymethylated cellulose was upped to 1.9 milliequivalents per gram. This compares with capacities from 0.4 to 0.6 milliequivalent per gram for the carboxymethyl celluloses now being used. The improved cation exchanger was made by cross linking cotton linters with formaldehyde, then carboxymethylating.

- Total capacity of phosphonomethylated cellulose was increased from 0.6 (first hydrogen) to 1.6 milliequivalents per gram. These results were obtained by cross linking with 1,3-dichloropropanol prior to phosphonomethylation with chloromethyl phosphonic acid and sodium hydroxide.

What's in a Hardwood Tree?

McGill chemists isolate polysaccharides present in white birch, find main hemicellulose is a 4-O-methylglucuronoxylan

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Cellulose Chemistry

Researchers at McGill University, Montreal, Que., have set themselves a lofty target. They're out to isolate and study all carbohydrates present in typical hardwood and softwood trees.

The study is fundamental, but it may lead to better knowledge on how to improve pulping techniques and produce new products from hemicelluloses.

Cellulose, the most common compound on earth, has been studied pretty thoroughly, but research on hemicellulose (polysaccharide components other than cellulose) has just gotten under way in the past decade since the advent of chromatographic techniques. Wood usually contains 40 to 50% cellulose, 20 to 30% lignins, and 20 to 30% hemicellulose.

Latest results of the McGill research program (now in its fifth year) come