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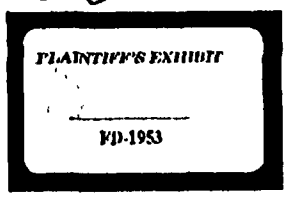

Intra Company

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Subject: Monthly Highlights for September, 1970, Chemical Engineering Department

Sodium-Sulfur Battery

Five conductive ceramic tubes of composition 9.25% Na_2O-0.25% Li_2O-90.5% Al_2O_3 were sintered to acceptable density and were successfully sealed simultaneously with glass into an alpha alumina reservoir for sodium in the preparation of a multi-cell battery.

The use of an inexpensive, $0.30/lb alumina has continued to be explored, and cells of 9.25% Na_2O-0.25% Li_2O-90.50% Al_2O_3 have operated satisfactorily on test for more than three months. Compositions of 9.5% Na_2O-0.7% Li_2O-89.8% Al_2O_3, containing the inexpensive Al_2O_3, have been tested in static sodium and in the short-time test with satisfactory results, and cells for long-time testing will be constructed.

In the continuing study of the ceramic degradation mechanism at high current density, the chemical composition at the fractured surface of degraded ceramics was an important unknown. The presence of grain boundary films of silica-, lead-, or phosphorus-rich material from raw material impurities and its reaction with sodium during electrolysis was a possible degradation process.

Samples of ceramic of composition 8.7% Na_2O-0.7% Li_2O-90.6% Al_2O_3 were, therefore, subjected to Auger Electron Spectroscopy analysis by personnel of the Metallurgy Department to determine the atomic species at the fractured surface of degraded and non-degraded ceramics. The absence of silicon, phosphorus and lead at the fractured surface was determined. The presence of metallic sodium at the fractured surface of degraded ceramics was detected. The presence of only ionic sodium in non-degraded samples was also detected. The presence of ionic sodium was characterized by the emission of yellow light which is characteristic of neutral sodium atoms (Na^+ ions combine with electrons from primary electron beam and are neutralized), whereas, at surfaces of degraded specimens, large sodium peaks were found in the Auger spectrum which were stable with respect to time and increasing primary beam currents. Further AES work is being done on partially degraded ceramics.

These AES results support the mechanism which explains degradation as the result of growth of surface cracks by stresses generated by the deposition of sodium metal into cracks more rapidly than the stresses can be dissipated by viscous flow of the sodium out of the crack. This mechanism predicts that metallic sodium would be present in cracks of degraded ceramics.

Exploratory experiments indicate that the failure mechanism of the ceramic is strongly temperature dependent. That means that the ability of the ceramic to carry current without damage increases considerably with temperature. In one set of experiments at 150°, 300° and 375°C, the critical current densities (causing significant resistance change) were: about 1, 1.5 and >4 A cm^{-2}, respectively.

Two tentative explanations are offered:

1) Because of higher resistance at lower temperatures, generation of heat, and consequently temperature gradients in the ceramic with resulting tensile stress on the surface are greater at lower than at higher temperatures.

2) The inhomogeneity of current distribution (between crystallites and grain boundaries) in the polycrystalline ceramic leads to local heating. Since the bulk conductivity grows faster with temperature, this effect becomes less pronounced with higher temperature.

International Power Sources Symposium, Brighton, England, 1970

Sodium Sulphur System. Discussions with the Electricity Council and British Railways indicate that significant progress is being made toward the successful development of the sodium-sulphur battery.

The Electricity Council has concentrated on the ceramic electrolyte, with both the LiO and MgO β-alumina compositions being investigated. Ionic resistivities of the order of 5-10 ohm-cm being obtained. A novel zinc sintering technique, in which tubes are passed through a hot zone, is used for preparing the ceramic electrolyte. Test cells have achieved several hundred cycles at 500 ma/cm^2. Cell failure has been primarily due to cracking of the ceramic tubes. A prototype battery, consisting of a number of individual cells, has been designed.

The British Railways have a large group and also support several university programs to complement their development programs. The physical properties of the sulphur-sulphide melt have been investigated, and extensive electrochemical studies are being done. The development of a low resistivity, long lived, ceramic electrolyte is, at present, being investigated. Both the

MgO and LiO doped ceramics are being evaluated. Major problems have been in sealing, corrosion and ceramic cracking. They believe that corrosion can be overcome using transition metal sulphides. A mechanical seal, using a graphite packing ("Grafail" Union Carbide), has proven satisfactory; other sealing methods however are being investigated. Ceramic failure, it is felt, can be overcome by the proper choice of ceramic composition and sintering.

The Companie General de Electricité in France is also investigating the sodium-sulphur system. They are using β-alumina tubes which have a life of about 400 hours at 1 amp/cm^2.

Sodium-sulphur studies are also being done at NASA, General Electric and at TRW.

Lead-Acid System. The major manufacturers in Europe and England have programs to develop an extensive needle-like crystal morphology in battery plate electrodes, similar to our own development in this area.

Oldham and Sons Ltd. in England expect to have a maintenance-free battery in about one year.

Other Systems. A high-energy density rechargeable Li organic electrolyte MnO_2 battery is reported to be under development at Mallory (USA).

Brake Fluid-Corrosion Properties

Although the normal value of the chloride ion concentration in brake fluid is about 10 ppm, some rather recent experience has shown that it can be as high as 100 ppm. The corrosion resistance of the brake system to such chloride variations has not been investigated with cars driven under known controlled conditions.

Therefore, a program has been initiated where the corrosion of the brake system in ten test cars will be determined as a function of the chloride concentration after one year of known road service.

Aluminum-Finned Radiators

The Scientific Staff is assisting Engine and Foundry Plant and Product Engineering in determining which of four approaches is best for the manufacture of aluminum-finned radiators. The four methods of joining the fins to the brass tubes are: zinc reaction flux treated aluminum with a lead-tin solder, untreated aluminum with a zonc-tine solder, copper-clad aluminum with a lead-tin solder, and bronzed aluminum (Alstan) with lead-tin solder. Radiators have been constructed by the first two methods. They have been metallurgically examined by the Metallurgy Department and are now being corrosion tested to determine the relative susceptibility to joint failure.

Phosphate Coatings--Chromic Acid Rinse

Recently published data have shown that the chromic acid rinse at the end of the phosphating operation can be eliminated without deleterious effects on corrosion protection if a heat treatment of the phosphate coating is substituted. The procedure is being recommended to Automotive Assembly and the Exterior Surface Finishing Committee for their consideration as a means of eliminating chromium-containing effluents. Salt spray data of scribed panels having the thermally treated coating show improved corrosion resistance over those with chromic acid rinsed coatings. Thermal analysis showed that the heating of panels to 180°C for several minutes involves the removal of half of the water of hydration (two moles of water/mole of phosphate). The heat treatment temperature is obtained by raising the phosphate coating drying oven

temperature by about 30-50°C. A laboratory evaluation of the heat treated coating is planned..

Quarter Panel Corrosion

About 20 percent of the 1968 through 1970 Ford cars in Florida are experiencing heavy corrosion of the quarter panel at the fuel filler tube area. The Service Engineering Department of Body Engineering has requested a procedure which will effectively prevent this type of corrosion on the warranty replacement parts. The corrosion failure is due to the entrapment of chloride-containing moisture in the quarter panel crevices formed at the panel-filler tube junction. The present practice is to replace the corroded section of the quarter panel by a new welded-in section. It has been recommended that the interior of this part by spray phosphated to Ford Spec. PL-53-33, and then spray painted with primer M6J49 and black topcoat M32J.

Cupola Corrosion

Engine and Foundry has requested assistance in determining the cause for the corrosion failure of the Cleveland Foundry cupola. The inner shell of the water-cooled section buckled through excessive corrosion. Recommendations for prevention of further failures will be made after the analysis of the problem is completed. A differential aeration cell failure mechanism is indicated.

Engine Cooling (with Mechanical Research Department)

It has been found in the literature that the addition of about 1 to 6% of certain organic compounds (e.g., butanol or methanol) to water can increase the maximum rate of boiling heat transfer by as much as 150%. A 50/50 mixture of water and ethylene glycol has been observed to behave in many respects as a

molecular compound, so that it might be expected that the additives would have similar effects on the limiting heat flux in that system. The use of such mixutres as engine coolants should result in substantial improvements in cooling of critical areas such as exhaust valve seats.

In a conventional cooling system, such additives could be lost by evaporation. A closed cooling system to prevent such loss has been conceived and described in an invention disclosure on these proposed engine coolant formulations.

Air Pollution from Brake Lining Wear (with Mechanical Research Department)

In order to obtain preliminary information and to establish test techniques, the cooling airstream passing over the brake during a dynamometer test of a production 10-inch drum brake was sampled with a membrane filter. Some asbestos fibers were observed on the filter by electroh microscope. A rough count indicated about 3×10^8 fibers per gram of wear dust collected. If verified by later tests, this would provide a very small concentration of fibers in the atmosphere when dispersed, using a realistic estimate of car population density. More precise tests are planned using more nearly isokinetic sampling conditions and a better characterized air sampling domain on disc and drum brakes.

A sample of drum dust from a vehicle was found by Technical Services Department to contain trace amounts of polynuclear aromatic compounds. Additional samples have been submitted for confirmation of this result.

Catalytic Emission Control

The effective service life of the catalytic emission control under evaluation can be significantly shortened through lead poisoning of the catalyst. Therefore, the use of lead-free gasoline is considered necessary for long-term

catalyst activity. Various procedures are being examined to prevent catalyst contamination through combustion of lead-containing fuel in cars equipped with the emission control. For example, detector-actuated systems designed to prevent filling of fuel tanks with "leaded" gasoline are being considered.

Invention Disclosure

A. E. Anderson and M. Weintraub, "Improved Engine Coolant System," File No. 70-391.

J. V. Petrocelli