I/EC BRIEFS

I/EC's March articles on:

- ☑ **Industrial Research and Development**
- ☑ **Process Design**
- ☑ **Chemical Engineering Fundamentals**
- ☑ **Unit Operations** ☑ **Unit Processes**
- ☑ **Commercial Chemical Development**

Short summaries to tell you...
what is reported
why it is significant

These Briefs are designed for clipping and
filing on 3 × 5 cards for ready reference.

---------- CLIP AND FILE FOR READY REFERENCE ----------

Staff-Industry Collaborative Report

EDTA, Ethylenediaminetetraacetic Acid

Although the textile industry remains the largest single user of
ethylenediaminetetraacetic acid, EDTA, producers are hopefully
eyeing such fields as agriculture, electroplating, mineral separations,
and food additives.

The first stepping stone to EDTA is its tetrasodium salt. There are
many routes to Na$_4$EDTA, but Geigy Chemical uses a one-step cyano-
methylation process, starting with ethylenediamine, hydrogen cyanide,
formaldehyde, and caustic. Hydrogen cyanide presents some tricky
handling problems, but the economies are worth the effort.

Reacting the Na$_4$EDTA with hydrochloric acid yields EDTA. By
starting with amines other than ethylenediamine, or by further reacting
EDTA, a host of different complexing agents can be made.

EARL V. ANDERSON and JOHN A. GAUNT

Ind. Eng. Chem. 52, 190–6 (1960)   **I/EC BRIEF**

Two Stage Process for Dialdehyde Starch Using Electrolytic Regeneration of Periodic Acid

In a two-stage process for producing dialdehyde starch, iodic acid in
aqueous solution is oxidized to periodic acid in an electrolytic cell,
and starch is oxidized by the periodic acid solution in a separate vessel.

Variables involved in starch oxidation were investigated, including
periodic acid purity, pH and temperature of reaction, concentration of
reactants, and recycling and purification of iodic acid for regeneration
to periodic acid and re-use. Satisfactory pilot-plant reaction condi-
tions were determined. The iodic acid solution resulting from reduc-
tion of periodic acid is recovered and recycled to the electrolytic cell
for reoxidation. Loss of iodic acid is less than 1 pound per 100 pounds
of starch processed.

Cost estimates indicate that dialdehyde starch of high oxidation and
alkali solubility can be produced economically.

V. F. PFEIFER, V. E. SOHNS, H. F. CONWAY, E. B. LANCASTER, S. DABIC,
and E. L. GRIFFIN, Jr.
Northern Regional Research Laboratory, U. S. Department of Agriculture,
Peoria, Ill.

Ind. Eng. Chem. 52, 201–6 (1960)   **I/EC BRIEF**

A Bench-Scale Crystallization Purification Column

Although fractional crystallization has long been recognized as a
powerful tool for laboratory purifications, it has not been as widely
used commercially as its potential value justifies, because crystalliza-
tion equipment has remained undeveloped and inefficient.

Starting with a new approach to equipment development, a counter-
current crystallization purification column was developed which has
operated successfully for over 5 years in a *p*-xylene plant. The new
equipment is so efficient and simple that it promises to expand the
industrial use of crystallization in separation and purification.

A bench-scale model of the column is described, with test procedures
for demonstrating its applicability for various systems. The ease with
which exploratory tests can be made should promote the development
of crystallization processes.

D. L. McKAY, G. H. DALE, and J. A. WEEDMAN
Phillips Petroleum Co., Bartlesville, Okla.

Ind. Eng. Chem. 52, 197–200 (1960)   **I/EC BRIEF**

Aluminum Chloride–Hydrocarbon Complex Catalyst in Isomerization of n-Heptane

Isomerization is increasingly important in refining processes for high
octane motor fuels. Aluminum chloride has been widely used for
isomerizing *n*-butane and *n*-pentane, but with heavier paraffins dis-
proportionation and catalyst degradation take place. In this study
n-heptane was isomerized by an aluminum chloride–hydrocarbon
complex catalyst. Isobutane was used to suppress disproportionation.

Nearly complete conversion of *n*-heptane to other products was
obtained in 15 minutes at 110° F. Side reactions decreased with
increasing isobutane concentration. At 5 moles isobutane per mole
n-heptane, an isoheptanes yield of 70% was obtained.

It is thought that the unstable *tert*-heptyl ion, formed from *n*-heptane
in an initial reaction, accepts a hydride ion from neighboring iso-
butane, and thus survives as isoheptane, rather than decomposing to
eventually yield disproportionation products.

H. J. HEPP and L. E. DREHMAN
Research and Development Department, Phillips Petroleum Co.,
Bartlesville, Okla.

Ind. Eng. Chem. 52, 207–10 (1960)   **I/EC BRIEF**

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Eastman Briefs
FOR MARCH
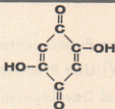
2,5-Dihydroxybenzoquinone

Form .... *orange yellow solid*
Melting point .... *216°C. (decomposes)*
Quality .... *technical grade*

From metal chelating to insecticide manufacture anyone interested in quinone compounds will find this one easy to work with—decidedly more stable than most and less irritating to skin and eyes.

Eastman Chemical Products, Inc.
Kingsport, Tennessee

B3
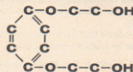
Hydroquinone Di-(β-Hydroxyethyl) Ether

Form .... *white solid*
Melting point .... *97-100°C.*
Water content .... *0.5% max.*
Hydroxyl number, mg. KOH/g. *555-565*

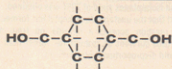Frankly, we've been amazed at the number of people who have listened to our story about this diol. We thought of it as a polyester intermediate. Beginning to suspect there's more than meets the eye. Polyurethane chain extender maybe?

Eastman Chemical Products, Inc.
Kingsport, Tennessee

B8

1,4-Cyclohexanedimethanol

Form* .... *solid*
Melting point .... *41-61°C.*
Isomer composition .... *30% cis; 70% trans*
Purity, % *99*

For the benefit of those who just came in, here's one of our more promising diol candidates for the polyester/polyurethane hall of fame.

*Supplied as 70% solution in methanol

**Eastman Chemical Products, Inc.**
Kingsport, Tennessee

B11

C—C—C—CN

n-Butyronitrile

Form .... *clear, colorless liquid*
Specific gravity, 20°/20°C. *0.7919*
Boiling range, 760 mm. .... *116.0-117.7°C.*
Purity, % *99*

We've been making isobutyronitrile for a number of years. It occurred to us the other day that somebody might be interested in the normal isomer. Prospects for early commercial production look favorable.

Eastman Chemical Products, Inc.
Kingsport, Tennessee

B23
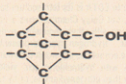
3-Methylnorcamphane-2-methanol

Form .... *clear, syrupy liquid*
Specific gravity, 20°/20°C. *0.9812*
Boiling range, 20-25 mm. .... *112-115°C.*
Color, APHA *10*

To keep our readers avidly awaiting the next issue of Eastman BRIEFS we feel called upon to offer something real gone now and then. Esters of this month's selection look interesting as synthetic lube viscosity improvers and as plasticizers.

Eastman Chemical Products, Inc.
Kingsport, Tennessee

B24

Chemicals Division
Eastman Chemical Products, Inc.
subsidiary of Eastman Kodak Company
Kingsport, Tennessee

C1

Please send more data on these chemicals:

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Catalyzed Hydrolysis of Sodium Borohydride

Kinetic studies of the cobalt-catalyzed hydrolysis of $NaBH_4$ have shown that the rate of evolution of hydrogen can be expressed by $-d(NaBH_4)/dt = 1.45 \times 10^{14} (CoCl_2)(NaBH_4)^{1/2} e^{-17500/RT}$. An increase in starting temperature of 5° C. decreases the time for complete reaction by about 50% in an adiabatic reaction.

The catalyst-forming reaction, as indicated by data for the reaction of excess $CoCl_2$ with $NaBH_4$, is $2CoCl_2 + 4NaBH_4 + 6H_2O \rightarrow (2Co \cdot B) + 3HBO_3 + 12^{1/2}H_2 + 4NaCl$.

Various quantities of hydrogen can be generated at different rates by controlling the concentration of catalyst. The catalyst requirements for any set of generation conditions are a function of several variables: initial reaction temperature, thermal losses, and time for homogeneous dispersion of the catalyst.

ARTHUR LEVY, JOHN B. BROWN, and CARL J. LYONS
Battelle Memorial Institute, Columbus 1, Ohio

I/EC BRIEF

Reductive Decomposition of Gypsum by Carbon Monoxide

When sulfur reserves are depleted, an economical process for manufacturing sulfuric acid from gypsum or anhydrite will be required. The first step will probably involve release of sulfur dioxide by sulfate decomposition.

Conditions were determined for the rapid and quantitative conversion of gypsum to sulfur dioxide and lime. Thus, when a gas mixture composed of 4% carbon monoxide, 20% carbon dioxide, 5% sulfur dioxide, and 71% nitrogen was passed over $-7 + 8$ mesh particles of gypsum heated to 2200° F., decomposition was rapid and complete. The rate of decomposition is a function of temperature, gas composition, mass velocity, and particle size. Side reactions producing calcium sulfide can be suppressed. The results suggest that reductive decomposition is a potential method for the commercial production of sulfur dioxide and lime, and hence sulfuric acid, from gypsum.

T. D. WHEELOCK and D. R. BOYLAN
Department of Chemical Engineering, Iowa State University of Science and Technology, Ames, Iowa

I/EC BRIEF

Steam Injection Heating

Steam injection is the fastest and simplest means of heating, where it is applicable.

Steam flows into the liquid in jets which are tangential to the cross section of liquid and nearly normal to the direction of liquid flow. The steam jets pulse in the low audio range. The average time of condensation is a few milliseconds.

Good design results in turbulent flow of a deaerated liquid past $^1/_4$-inch pads, through which steam flows at sonic velocity.

ARTHUR I. MORGAN, Jr., and ROBERT A. CARLSON
Western Regional Research Laboratory, U. S. Department of Agriculture, Albany, Calif.

I/EC BRIEF

Effect of Surface on Vapor Phase Oxidation and Nitration of Propane

Nitration experiments with propane and nitric acid, in some cases using oxygen as an additive, and oxidation experiments with propane and oxygen were performed in molten salt and tubular reactors. The conversions and products obtained varied with the reactor used indicating that surface effects are important for these reactions. Some surfaces suitable for oxidation reactions tend to suppress nitration reactions. A suitable surface is apparently required to initiate the low-temperature oxidation reaction. A molten salt surface is not satisfactory for the low-temperature oxidation reaction or for increasing nitration conversions when oxygen is used as an additive. The initiating steps of the high-temperature oxidation and the nitration reactions, however, probably occur in the gas phase. Terminating steps of the chain mechanisms presumably occur on the surface for all types of reactions studied.

LYLE F. ALBRIGHT, STEPHEN A. LOCKE, DONALD R. MacFARLANE
Purdue University, Lafayette, Ind.

GERALD L. GLAHN
University of Oklahoma, Norman, Okla.

I/EC BRIEF

Reprocessing Plutonium Reactor Fuel. Removal of Fission Product Elements by Slagging

The applicability of oxide and chloride slagging for removing fission products from plutonium reactor fuel has been investigated.

Rare earth elements are removed effectively by either method, but a comparison of the purification, reaction times, and yields indicates that chloride slagging is the preferred method.

L. J. MULLINS, J. A. LEARY, and W. J. MARAMAN
Los Alamos Scientific Laboratory, University of California, Los Alamos, N. M.

I/EC BRIEF

Removal of Molten Sodium from Reactor Coolant Systems

There are twin problems, the safe and facile removal of inaccessible 100-pound quantities of sodium metal from large containers and the removal of pound lots of sodium from small systems in inaccessible locations.

Laboratory scale (4-inch pots) and mock-up runs (1- and 2-foot pots) have shown that molten sodium may be removed from closed containers safely and easily. Application has been extended to small piping systems without hazard.

The tests show that large industrial vessels containing liquid sodium metal may be safely drained of their contents by physical means. Sodium in piping is handled in similar manner. No explosive gases, liquids, or solids are formed. The liquid suggested, HB-40, has a flash point of 170° to 180° C., and operating conditions are not above 140° C.
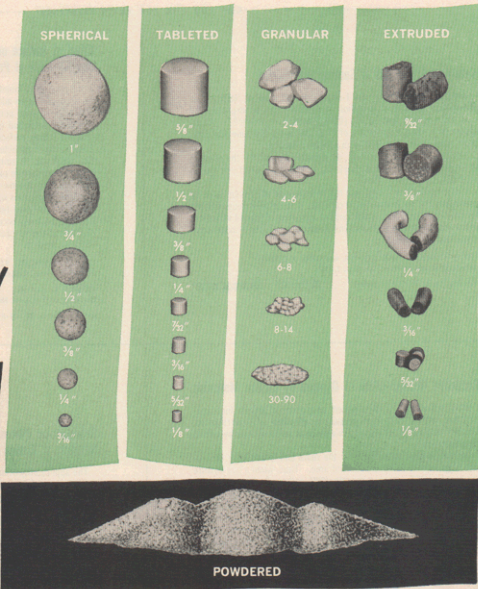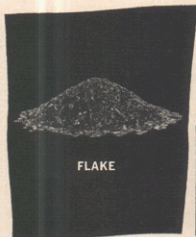
LOUIS SILVERMAN and ROBERT A. SALLACH
Atomics International, A Division of North American Aviation, Inc., Canoga Park, Calif.

I/EC BRIEF

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Methylcellulose in Water-Retentive Hydraulic Cements

Mortars and pointing compounds that could be applied directly over dry surfaces and to dry tile were required by the ceramic tile industry.

Up to 2% methylcellulose gave water-retentivity to the aqueous phase of hydraulic cement compositions and allowed their effective use under dry conditions and in very thin bonding and joining layers. Bond strengths in excess of the highest attainable by the conventional methods and compositions were obtained.

During the past 3 years, formulations of this type have been used to set millions of square feet of ceramic tile and are presently used to install about 20% of the total ceramic tile footage in this country.

HERMAN B. WAGNER
Tile Council Research Center, Box 326, Princeton, N. J.

Ind. Eng. Chem. 52, 233–4 (1960)   I/EC BRIEF

Synthetic Rubber Production. Chelating Agents in Sulfoxylate Polymerization

Chelating agents based on (ethylenedinitrilo)tetraacetic acid (EDTA) have become important components in modern, peroxide-catalyzed, cold rubber production systems, yet little has been published concerning effects on conversion rate of changes in chelant or chelant levels.

Polymerization studies on a typical sulfoxylate system showed that aminopolycarboxylic acid chelants other than EDTA were incapable of sustaining the polymerization reaction. However, concentration and purity of EDTA based chelating agents could be changed markedly with little adverse effect on the conversion rate.

The results illuminate an area where alterations requiring minimum developmental activity by the rubber producer could result in substantially more efficient utilization of chelant.

A. K. PRINCE and R. D. SPITZ
The Dow Chemical Co., Midland, Mich.

Ind. Eng. Chem. 52, 235–8 (1960)   I/EC BRIEF

Delayed Action Accelerators for Vulcanizing Rubber. Preparing N-Alkyl- and N-Cycloalkylbis(2-benzothiazolesulfen)amides

Optimum conditions have been developed for preparing N-alkyl- and N-cycloalkylbis(2-benzothiazolesulfen)amides, delayed action accelerators for vulcanizing rubber, by the reaction of 2 moles of 2-benzothiazolesulfenyl chloride with 3 moles of a primary amine.

Products having delayed action properties approaching those of the pure compounds are obtained in 94–99% yield by concurrent addition of the reactants and by lowering the reaction temperature or reducing the time for addition of the amine to the sulfenyl chloride. These conditions suppress the attack of the sulfenyl chloride on the bis(2-benzothiazolesulfen)amide and the intermediate mono-2-benzothiazolesulfenamide.

The addition of the sulfenyl chloride to the amine gives poor results, even at a low temperature; an explanation is given.

NORMAN K. SUNDHOLM
Naugatuck Chemical Division, United States Rubber Co., Naugatuck, Conn.

Ind. Eng. Chem. 52, 239–40 (1960)   I/EC BRIEF

Burning Selenium and Barium Peroxide Powders

The need for more closely timed delay fuses may be satisfied by more fundamental knowledge of the behavior of metal powder–oxidant systems.

Preheating mixtures of selenium and barium peroxide caused the heat output to decrease, the burning rate to pass through a maximum, and the activation energy for firing to pass through a shallow minimum, suggesting a multiprocess reaction.

Specified preheating can give a better control over the burning rate of these mixtures.

LEWIS B. JOHNSON, Jr.
Research Laboratories for the Engineering Sciences,
University of Virginia, Charlottesville, Va.

Ind. Eng. Chem. 52, 241–4 (1960)   I/EC BRIEF

How to Predict Flammability in Ozonization Reactions

In the past, ways to minimize the hazard of flame and explosion in organic ozone reactions were either unknown or misunderstood. A method is described for evaluating the safety of an ozonolysis reaction and some data are presented on the effect of temperature and water in preventing spark-induced flame and explosion in ozonization reactions.

Water can be used to provide evaporative cooling, remove the heat of ozonolysis, and minimize reaction "hot spots." The amount of water required to prevent spark-induced flame and explosion is small compared to the amount required for evaporative cooling. Temperature control in some anhydrous reactions is necessary if flame is to be avoided. Ozone concentration, up to 9% by weight in oxygen, and the presence of ozonized products in the reaction mixture do not affect flammability limits.

W. E. CROMWELL
The Welsbach Corp., Philadelphia, Pa.

Ind. Eng. Chem. 52, 245–6 (1960)   I/EC BRIEF

Permeability to Water of Partially Saturated Glass Fiber Beds

In many commercial fibrous material processes, such as suction dewatering, pressing, and drying of paper pulp, relative liquid permeability is an important and often controlling factor. Glass fibers provided a geometrically simple medium for a basic study of the permeability to liquids of partially saturated fibrous systems.

Compared with several different granular media of comparable pore size, glass fiber beds show a more rapid fall-off in water relative permeability with decreasing saturation. With a quantitative expression derived from a modified Kozeny-Carman equation, relative permeability can be defined in terms of four system variables: usual pore size distribution, hydraulic tortuosity, Kozeny shape factor, and a shape factor characteristic of the surface to volume ratio of the pores.
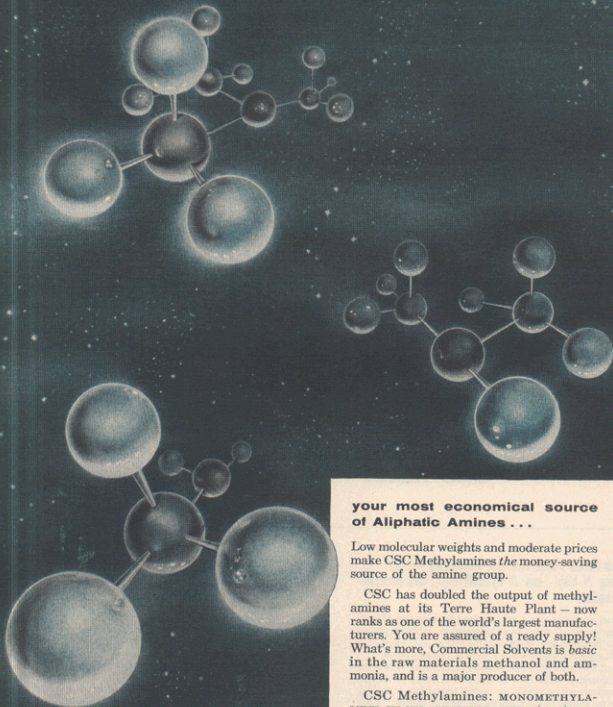
JOSEPH D. PARKER
The Institute of Paper Chemistry, Appleton, Wis.

Ind. Eng. Chem. 52, 247–50 (1960)   I/EC BRIEF

THE METHYLAMINES!

Prediction of Multistage Solvent Extraction Operation from Limited Data

It is desirable to be able to relate performance of a solvent extraction system to easily measured parameters.

Distribution isotherms for solvent extraction systems are often curvilinear. In many cases this curvature is due to a diminishing number of available extraction sites in the solvent as the amount of extracted material increases. This situation can be described by a Langmuir adsorption isotherm, and multistage behavior of such systems can be predicted by solving the McCabe-Thiele diagram.

Extraction recovery has been computed for a range of conditions and the data are presented as a series of curves. The behavior of counter-current multistage extraction systems can be predicted with these curves.

DAVID A. ELLIS
Western Division, Research Department, The Dow Chemical Co., Pittsburg, Calif.

I/EC BRIEF

Statistical Theories of Turbulence in Predicting Particle Size in Agitated Dispersions

Present methods for the scale-up of agitated systems from pilot plant to large scale poses many problems. Older methods commonly employed for scale-up are based on either the empirical principle of equal energy input per unit volume, or dimensional analysis. Both have their limitations. The former lacks a basic theory which might otherwise explain its failure to give consistent results. Dimensional analysis requires a great deal of accurate process data over a wide range of conditions in order to be useful.

A new approach to the analysis of dispersions in stirred tanks has been developed. The statistical theory of local isotropy developed by Kolmogoroff sheds new light on this problem. It provides an excellent theoretical basis for the treatment of mixing processes and is also applicable for describing the behavior of turbulent flow as well as predicting particle size distribution in agitated dispersions.

REUEL SHINNAR and JAMES M. CHURCH
Columbia University, New York, N. Y.

I/EC BRIEF

Unit Operations Reviews

Fundamentals of Chemical Engineering Review