Finished carbon monoxide shift catalyst looks like this. Tablet size is $^3/_8$ or $^1/_4$ inch, approximate surface area is 100 square meters per gram

I/EC STAFF INDUSTRY COLLABORATIVE REPORT

Catalyst Manufacture

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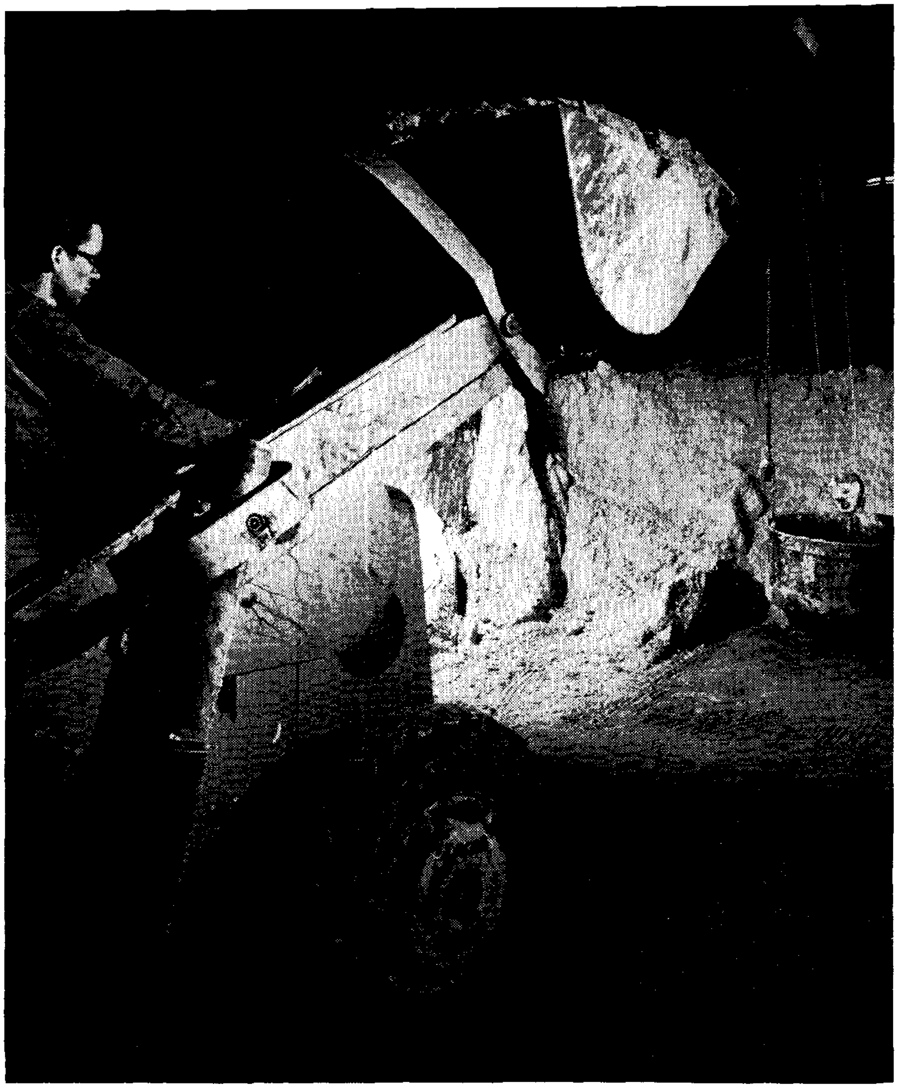
A variety of equipment is required to make catalysts—from stainless steel tanks to rotary tabletting presses. If you are in the chemical manufacturing business, I/EC's Staff-Industry Report may be a good shopping guide for equipment for your plant

Considering that for years catalysis was a "by the seat of the pants" science, catalysts' ubiquity in industry is nothing short of amazing. Today, catalytic processes are used to make an almost endless list of products—gasoline, plastics, synthetic and "natural" synthetic rubber, methanol and higher alcohols, ammonia, nitric acid, and synthesis gas are but a few. The scope of catalytic reactions includes reforming, hydrogenation, dehydrogenation, polymerization, condensation, metathesis, desulfurization, and others. And those much heralded polymers, polyethylene and polypropylene, are but merely Johnny-come-latelies



Ferrous sulfate is stored in bulk like this, then scooped up and transported to washing tanks

into the large family of industrial catalytic processes.

Although catalysis first started as a hit-or-miss technique, its premier position today is due to an ever widening scientific discipline which has been built about catalysts and catalytic processes. Early in the 1900's, catalyst chemists had to depend mostly on empirical correlations (and on a good many hunches) while using relatively sparse literature data (*3*). Today, though, there is a greater understanding of the detailed mechanisms by which catalysts function. And as with the science of catalysis, so the manufacture of catalysts rests on a sounder scientific and engineering basis.

Today's modern catalyst manufacturing plant is an enviable example of a study in unit operations. It is a plant in which a variety of catalysts are made, each tailored to a specific purpose. Gone forever is the day when a catalyst plant operator had no more than a pot and a prayer to work with. Now, such a plant is geared to volume production of uniform material using the latest innovations in process equipment and relying heavily on research, development, and stringent quality control.

Among the industrial organizations which have pioneered both catalytic process and catalyst manufacturing techniques is Girdler Catalysts, Louisville, Ky., a part of the Chemical Products Division of Chemetron Corp. The company's catalyst manufacturing activity dates back to 1942 when catalysts were made for use in gas process plants designed and constructed by the original Girdler Corp. (now a part of Chemetron). These plants include those for steam-hydrocarbon reforming, ammonia and nitrogen fertilizers, carbon dioxide, carbon monoxide, synthesis gases, sulfur recovery, poly(vinyl chloride), polyethylene, calcium carbide, synthetic rubber, and others. In recent years, catalysts of many other kinds have been made.

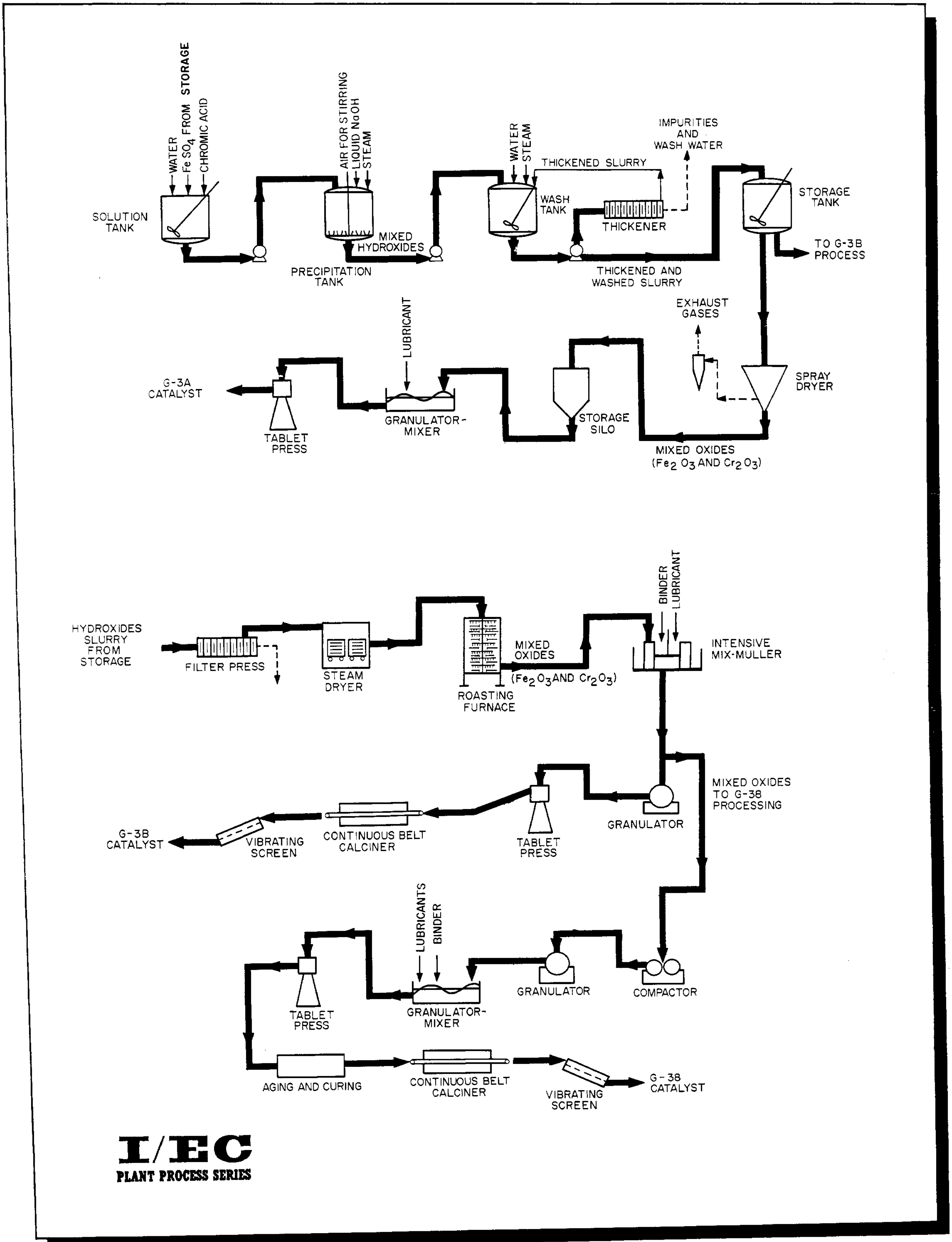
General Methods for Making Catalysts

Catalyst production in general can be divided into four methods (*4*). These include:

- Precipitation and gel formation—chemically the two are very similar, although physical characteristics of the final product are different. Precipitation is often used in making single and multiple component catalysts. The technique is used with materials like oxides, sulfides, carbonates, and phosphates. On a commercial scale, aqueous solutions of the desired constituents are used. Gel formation is suited to making those catalysts whose major components are hydrous oxides. Catalysts containing silica or alumina are most amenable to gel formation.

- Impregnation methods—one of the simplest ways to produce a catalyst. Impregnation of a support involves using a soluble compound dissolved in a liquid (usually water). It is also possible to do vapor phase impregnation if the desired

Looking into washing tank where mixed ferrous and chromous hydroxides are washed



Flowsheet for the manufacture of catalysts, Girdler Catalysts, Chemical Products Division, Chemetron Corp., Louisville, Ky.

constituent can be found in a volatile compound. Supports can be pelleted, granular, or powdered solids.

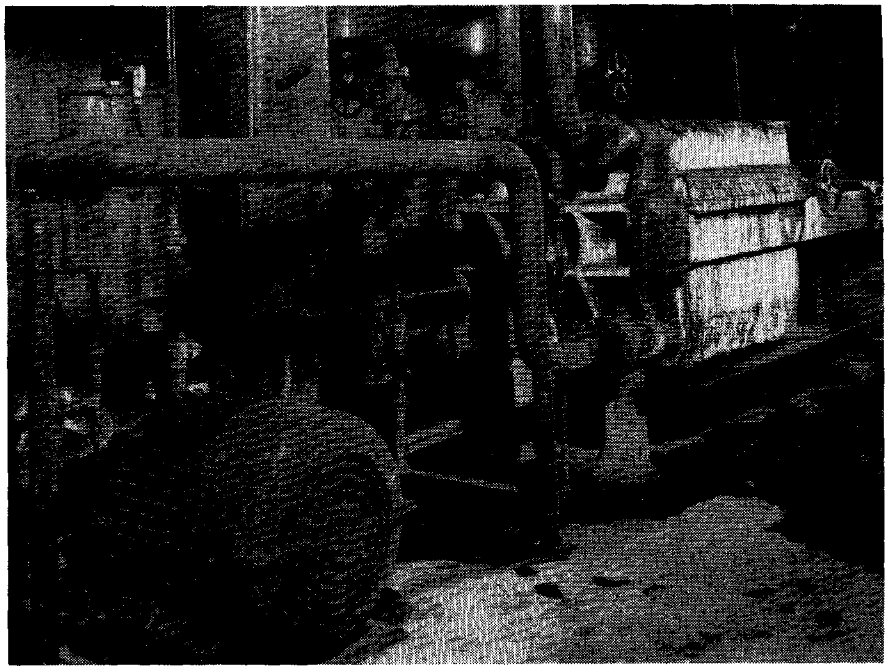
● Wet mixing—components may be hydrogels, hydrous precipitates, dried materials, or a combination of dried materials with one of the others. Ball mulling is commonly used to prepare small batches.

● Miscellaneous methods—these include thermal fusion like that used to make fused iron catalyst for synthesis of hydrocarbons and ammonia, chemical reactions such as metathesis (which is also involved in precipitation or gelation techniques), decomposition, oxidation and reduction, and others. Evaporation of one metal from another is still another method by which some catalysts may eventually be made commercially.

Unit operations involved in almost all catalyst manufacturing include:

- ▶ Washing to remove impurities
- ▶ Drying
- ▶ Forming or sizing
- ▶ Calcining and activating.

Variations in any of these steps may affect the catalyst's activity. Conditions for each operation vary widely depending on the composition, activity desired, granule size, porosity, and many other considerations.



Thickener press has 30 chambers, is equipped with a nylon cloth

The Girdler Catalysts' Organization

A characteristic of Girdler Catalysts' plant in Louisville is its versatility, which enables making many kinds of catalysts. A fair share of the company's business is based on custom or specialty (less than 1,000,000 pounds a year) catalysts although the firm considers itself mainly a stock catalyst company. On a poundage basis, Chemetron claims that it produces as much specialty catalysts—exclusive of petroleum cracking and naphtha reforming catalysts—as any other manufacturer today.

Export sales make up an important part of the business. Recently Chemetron announced the formation of an affiliated company in Germany to handle its entire line of catalysts in Europe, the Near East, Africa, and other areas in order to be in a better position to serve its expanding overseas market.

Girdler stock catalysts include those used for production of synthesis gases and hydrogen, hydrogenation, steam-hydrocarbon reforming, desulfurization, selective hydrogenation of acetylenic compounds, and oxygen removal. The company also has a series of catalysts which are in one stage of development or another. These are available in small quantities for further investigation.

Spray dryer's lower portion and control panel. Dryer is natural gas-fired, can operate at 1100° F., and can generate 4,000,000 B.t.u.

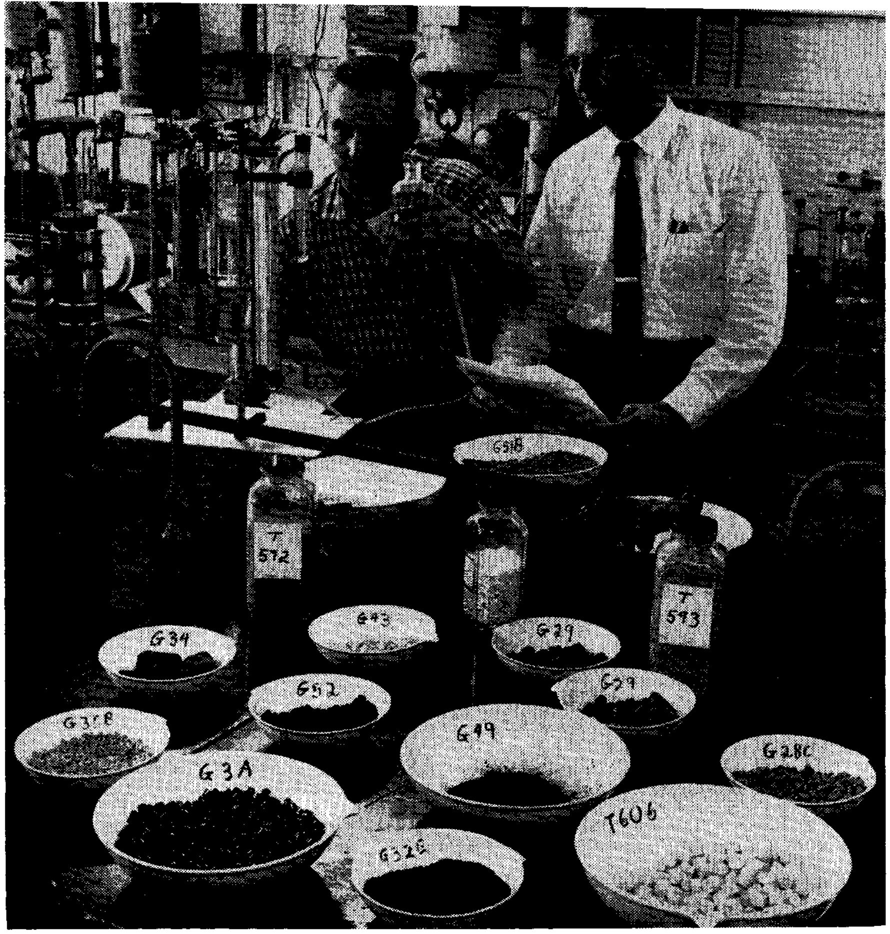
CO Shift Catalysts Major Items

About 70% of the company's stock catalyst business is made up of its carbon monoxide shift catalysts, nickel hydrocarbon-steam reforming catalysts, and selective acetylene hydrogenation catalysts. This report deals with the stepwise manufacture of three varieties of carbon monoxide shift catalysts (*2*). The three, known as Girdler G-3A, G-3B, and G-38 catalysts, are all similar but are tailored for use under different process conditions. In addition to their making up one of the company's main product lines, production of the three catalysts uses most of the unit operations found in the Louisville plant.

These three products are chromium promoted iron oxide catalysts, as are most of the widely used carbon monoxide shift catalysts (*7*). G-3A is used in hydrogen and ammonia synthesis gas plants for converting carbon monoxide and steam at high temperatures to carbon dioxide and hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The catalyst is not permanently affected by limited exposure to liquid water,



Quality control consists of chemical analysis, crushing strength, crystalline form, and other tests performed at various stages of the catalyst manufacturing process

says Girdler Catalysts, nor is it as sensitive to sulfur compounds as are some other shift catalysts. Charges of G-3A have been in service for over nine years, the company claims.

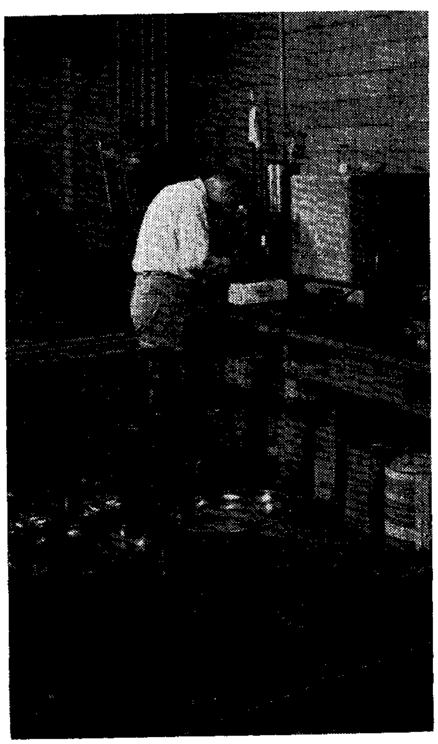
In commercial use at or near atmospheric pressures, G-3A is used in a temperature range of 700° to 850° F. and space velocities between 300 and 1000. At higher pressures, above 10 atm., the catalyst can be used between 600° and 750° F. with space velocities of 300 and 1000. Or, temperatures can range from 750° to 850° F. at space velocities between 800 and 2500.

G-3B is similar to G-3A but is designed to meet the rigorous conditions imposed by the operation of partial oxidation processes used to generate synthesis gases. The third "G" carbon monoxide shift catalyst, G-38, is also essentially the same catalyst; physically stronger but somewhat lower in activity. Its main use is in some newer processes where pressures and temperatures are higher, causing more rapid aging of the catalyst.

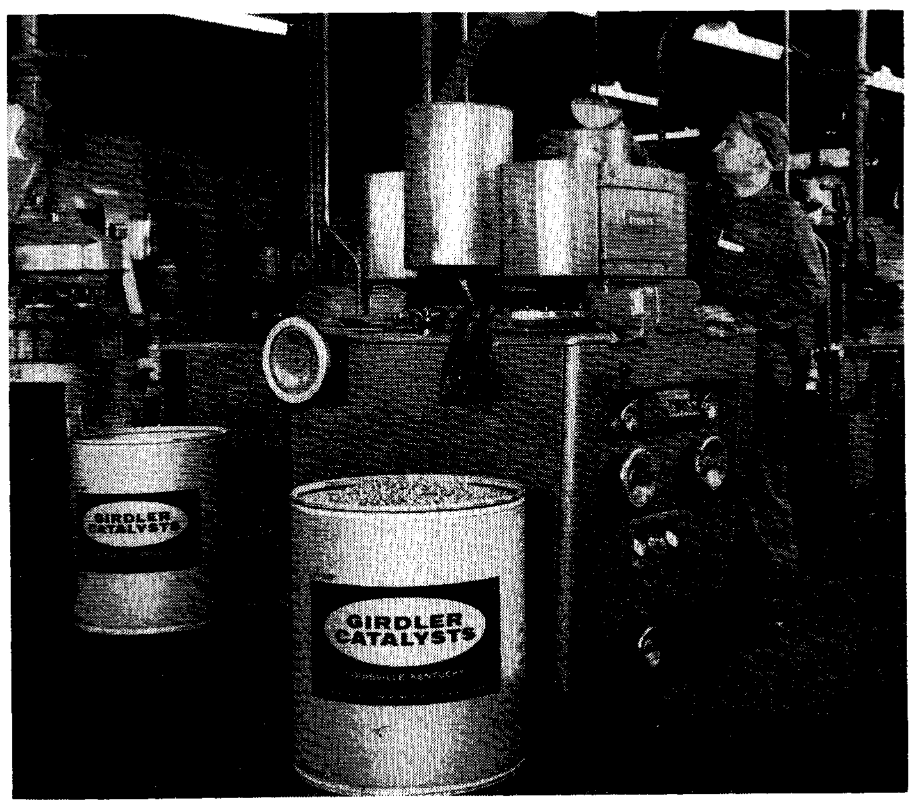
The catalysts are usually produced in tablet form, sizes from $^3/_8$ to $^1/_4$ inch. Average apparent density is between 75 and 88 pounds per cubic foot, depending on the product. Approximate surface area is 100 square meters per gram.

Catalyst Plant and Process

Girdler Catalysts' Louisville plant is



Modern catalyst production calls for strict quality control. Tests performed in this control laboratory include chemical analysis, crushing strength, and crystalline form determinations



Hi-speed, rotary tabletting presses can turn out 100,000 pounds of catalyst tablets each day laid out into three distinct operating areas plus warehouse and raw materials storage space. Operations include precipitation and washing, calcining, drying and reducing, and preforming and forming. Each area takes up about 200 × 62 feet of floor space in the one-story building. The plant was enlarged by 37% during the summer of 1957.

Major raw materials for Girdler carbon monoxide shift catalysts are ferrous sulfate and chromic acid. The iron salt and the acid are first dissolved in water in a 1000- or 2000-gallon stainless steel solution tank built by local fabricators to company specifications. Tank contents are stirred constantly.

When solution is complete, the iron sulfate–chromic acid solution is pumped to precipitation tanks made of iron; each tank is air agitated and has a capacity of 4000 gallons. Depending upon the amount of catalyst being made, from 3 to 6 of these tanks are used. Sodium hydroxide is metered into the precipitation tank and live steam is used to heat the contents. Coprecipitation takes place at this stage resulting in a slurry of mixed ferrous and chromous hydroxides.

Washing the mixed precipitates with water is the next step. The slurry is pumped into a third set of iron 4000-gallon tanks equipped with turbine-type agitators. One such tank can handle three batches of precipitate. Tank contents for this washing operation are also heated with steam. Washing of the hydroxides gel is done until analysis of the wash water shows no foreign materials.

The hydroxides mixture is then pumped through a 30-chamber thickener press (*12E*) equipped with a nylon cloth. After passing a quality control test—at this point wash water composition is determined—the thickened precipitate is pumped into an agitated storage tank which is similar to the washing tanks. From the storage tank the slurry is routed either to G-3A catalyst manufacture or to G-3B and G-38 processing.

G-3A Processing. When making this particular carbon monoxide shift catalyst, the thickened slurry containing mixed ferrous and chromous hydroxides is pumped from the storage tank to a spray dryer and collection system (*1E*).

The dryer, 10 feet in diameter, is made of an iron alloy and uses disk atomization. The slurry feeds into the disk which is shaped like an upside-down saucer. Centrifugal force throws the slurry over the edge of the disk while it is spinning at from 9000 to 20,000 r.p.m. Uniform droplets are formed when the material goes over the disk's edge. Natural gas-fired, the dryer is capable of operating at 1100° F. and can generate 4,000,000 B.t.u. The unit handles from 300 to 500 pounds of the mixed hydroxides per hour.

In the dryer, the hydroxides are oxidized to ferric and chromic oxides. Crystalline form of the iron can be controlled in the dryer by changing the temperature. The spray-dried oxides are collected and stored in a steel storage silo that can hold about 100,000 pounds of the material. Control tests including sizing, moisture content, and chemical composition are done on the oxide mixture coming from the spray dryer.

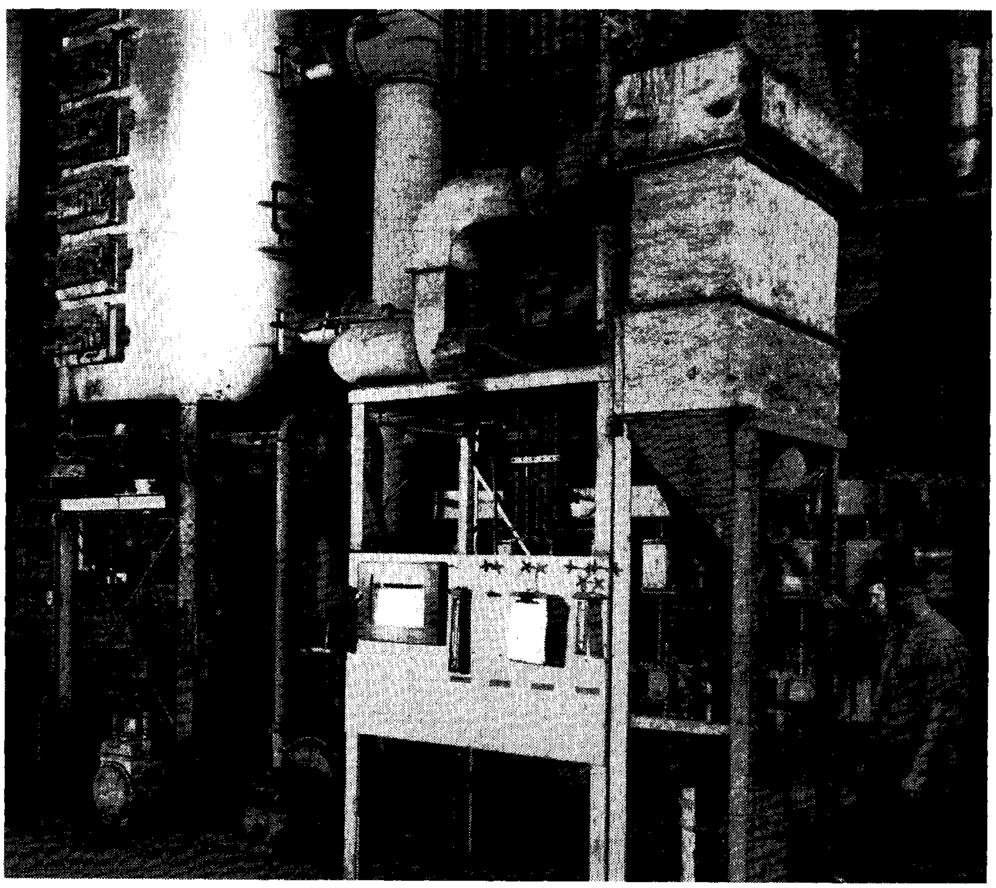
The catalyst finishing operation involves running the spray-dried oxides mix through a stainless steel granulating mixer (*15E*) where it is coated with a lubricant. The mixture is then pelleted on rotary tabletting presses (*2E, 16E*). Girdler Catalysts' battery of tabletting machines can turn out 100,000 pounds of catalyst pellets a day in a size range of $^3/_8$ to $^1/_2$ inch. Crushing strength of the tablets is determined and the finished catalyst stored in fiber drums.

G-3B Catalyst. In making this catalyst, which is similar to G-3A but a more rugged one, the spray-drying step is bypassed. Instead, the mixed hydroxides slurry is pumped from the storage tank to recessed plate filter presses (*13E, 14E*). After filtering, the filter cake is dried in a tray-truck feed conditioning steam dryer (*10E, 11E*).

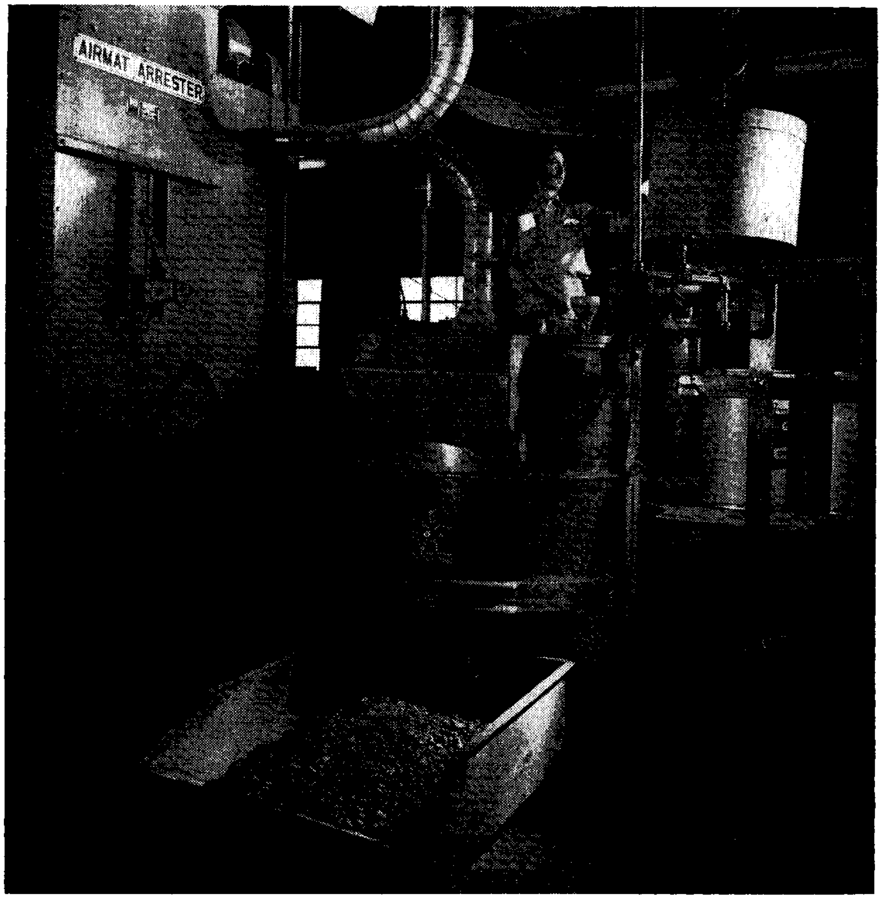
Then the steam-dried mixed precipitate is transported to an oxide roasting furnace (*9E*). This furnace is 54 inches in diameter, has 8 hearths, and may be operated at temperatures up to 1800° F. Air is the oxidizing atmosphere. Oven operation can be either continuous or on a batch basis. A check of crystalline form and chemical content is made at this point.

The oxides are next taken to an intensive mix-muller (*7E*). Here, binders and lubricants are added and the mixture is sent to the granulators (*4E*). As with G-3A catalyst, tabletting follows granulation; but instead of packaging the tablets as they come off the presses, they first undergo a calcining step. Calcining is done on a continuous belt, natural gas-fired calciner (*6E*) at 750° F. The pellets coming off the calciner are screened on a two-deck vibrating screen (*8E*) or on an oscillating screen (*3E*). Finished G-3B catalyst is packed in fiber drums and stored for shipment.

G-38 Catalyst. Up until the binders



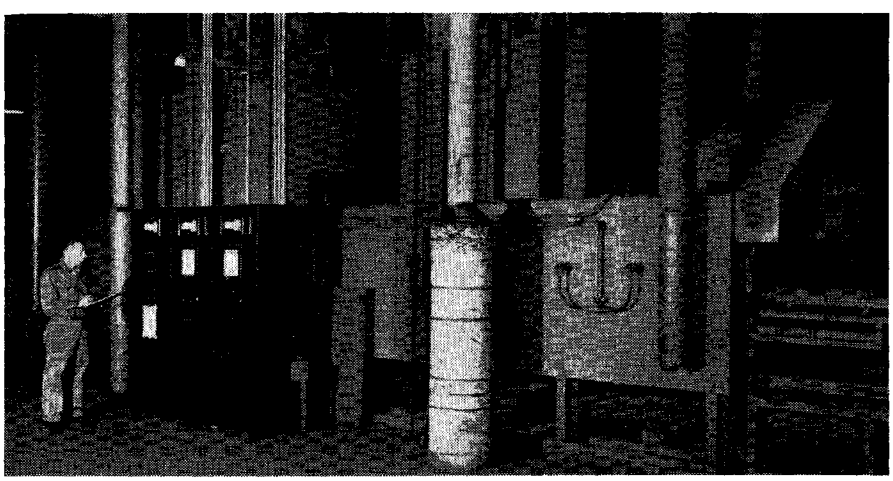
Oxide roasting furnace is 54 inches in diameter, has 8 hearths, and operates at temperatures up to 1800° F.



The intensive mix-muller, where binders and lubricants are added to the mixed oxides, is unit operation's version of a mortar and pestle

and lubricants are added, this process is the same as for G-3B. The mixed oxides from the mix-muller earmarked for G-38 are then compressed in compactors (*5E*, *17E*). Resulting briquets are sent through the granulating mixers, where a binder and additional lubricants are added. Tabletting is done as with the others, followed by a rigid aging and curing process. Calcining and packaging operations are the same as with G-3B.

In addition to the unit operations used in making the carbon monoxide shift catalyst line, Girdler Catalysts has additional equipment that is used for manufacturing other types of catalysts. Some of this equipment is so specialized that it is in use no more than three months out of a year.



Used in making the G-3B and G-38 carbon monoxide shift catalysts, this natural gas–fired calciner operates at 750° F.

New Catalysts in the Offing

Several new catalysts as well as some refinements of the current product line are under way. Recent additions to the company's catalyst line include a non-pyrophoric reduced nickel catalyst (for application in areas where sponge nickel has been used) and an improved nickel on kieselguhr catalyst for selectively hydrogenating vegetable and animal fats.

Girdler Catalysts' new product hopes rest heavily on its research staff which is being expanded, while a new research building is in the planning stage. And a continuing research function consists of adding to existing catalysis data, thereby divorcing the science from the art as completely as possible.

Acknowledgment

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(1) Atwood, K., Arnold, M. R., Ind. Eng Chem. **45**, 424 (1953).
(2) Christian, D. C., Reed, R. M. (to Girdler Co.), U. S. Patents **2,602,020** (July 1, 1952); **2,662,063** (Dec. 8, 1953).
(3) Emmett, P. H., "Catalysis," vol. **1**, p. iii, Reinhold, New York.
(4) *Ibid.*, pp. 315–21.

Processing Equipment

(1E) Bowen Engineering Co., North Branch 3, N. J., spray dryer and collection system.
(2E) Arthur Colton Co., Detroit 7, Mich., rotary tabletting presses.
(3E) Day, J. H., Co., Div. of Cleveland Automatic Co., Cincinnati 12, Ohio, oscillating screen.
(4E) Fitzpatrick, W. J., Co., Chicago 7, Ill., granulators.
(5E) Komarek-Greaves and Co., Chicago 18, Ill., compactors (briquet presses).
(6E) Lindberg Engineering Co., Chicago 12, Ill., continuous belt calciner.
(7E) National Engineering Co., Chicago, Ill., intensive mix-mullers.
(8E) *Ibid.*, two-deck vibrating screen.
(9E) Nichols Engineering & Research Corp., New York, N. Y., oxide roasting furnace.
(10E) Proctor & Schwartz, Inc., Philadelphia 20, Pa., tray-truck feed conditioning steam dryer.
(11E) Ross, J. O., Engineering Corp., New York 22, N. Y., steam dryer.
(12E) Shriver, T., & Co., Harrison, N. J., 36-inch thickener press with nylon cloths.
(13E) *Ibid.*, 30-inch recessed plate filter press.
(14E) Sperry, D. R., & Co., North Aurora, Ill., recessed plate filter press.
(15E) Stokes, F. J., Corp., Philadelphia 20, Pa., stainless steel granulating mixers for lubricant coating.
(16E) *Ibid.*, rotary tabletting presses.
(17E) *Ibid.*, compactors (briquet presses).