

# FERRIC OXIDE

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Ferric oxide ( $\text{Fe}_2\text{O}_3$ ) occurs naturally and is often used as a red pigment employed in paints and primers, as well as in rubber formulation. Because of durability, the iron oxide pigments are used in barn and freight car paints. The synthetic pigment is made by heating iron sulfate.

*Venetian red* is a mixture of ferric oxide with up to an equal amount of the pigment extender, calcium sulfate. This pigment is manufactured by heating ferrous sulfate with quicklime in a furnace. Venetian red is a permanent and inert pigment, particularly on wood. The calcium sulfate content, which furnishes corrosion-stimulating sulfate ions, disqualifies this pigment for use on iron.

*Indian red* is a naturally occurring mineral whose ferric oxide content may vary from 80 to 95%, the remainder being clay and silica. It is made by grinding hematite and floating off the fines for use.

# FERROCYANIDE BLUE

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Ferrocyanide blue occurs in various shades known as Prussian blue, Chinese blue, muon blue, bronze blue, Antwerp blue, and Tumbull's blue. These names have lost much of their original differentiation; the more general term *iron blues* is preferred.

These pigments are manufactured by treating ferrous sulfate ( $\text{FeSO}_4$ ) solutions (sometimes in the presence of ammonium sulfate) with sodium ferrocyanide, giving a white ferrous ferrocyanide, which is then oxidized to ferric ferrocyanide,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]$ , or to  $\text{Fe}(\text{NH}_4)[\text{Fe}(\text{CN})_6]$  by different reagents such as potassium chlorate, bleaching powder, and potassium dichromate. The colloidal pigment is washed and allowed to settle to enhance separation, since filtration of the colloidal solid is difficult.

Iron blues possess very high tinting strength and good color performance and the relative transparency of these pigments is an advantage in dip-coating foils and bright metal objects, and for colored granules for asphalt shingles. They cannot be used in water-based paints because of their poor alkali resistance.

# FERTILIZERS

Fertilizers provide the primary nutrients (nitrogen, phosphorus, and potassium) for vegetation and are manufactured by a variety of processes (Fig. 1) and from a variety of raw materials (Fig. 2). The usual sources of nitrogen are ammonia, ammonium nitrate, urea, and ammonium sulfate. Phosphorus is obtained from phosphoric acid or phosphate rock and potassium is available from mined potassium chloride or potassium sulfate or it is obtained from brine.

| Raw materials  | Primary chemicals | Derived chemicals  |
|----------------|-------------------|--------------------|
| Air            | Ammonia           | Ammonium sulfate   |
| Hydrogen       | Ammonia           | Urea               |
|                |                   | Ammonium nitrate   |
| Phosphate rock | Phosphoric acids  | Ammonium phosphate |
|                |                   | Superphosphates    |

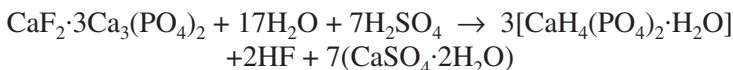
**FIGURE 1** Routes for the manufacture of fertilizers.

| Raw materials           | Primary product | Secondary product   |
|-------------------------|-----------------|---------------------|
| Wood                    | Ammonia         | Urea                |
| Lignite                 |                 | Ammonium nitrate    |
| Coal                    |                 | Ammonium sulfate    |
| Hydrogen                |                 | Ammonium chloride   |
| Coke oven gas           |                 | Ammonium phosphates |
| Natural gas             |                 |                     |
| Liquefied petroleum gas |                 |                     |
| Refinery gas            |                 |                     |
| Naphtha                 |                 |                     |
| Fuel oil                |                 |                     |
| Bunker C oil            |                 |                     |

**FIGURE 2** Raw materials used for fertilizer manufacture.

Fertilizers may contain all three primary nutrients, in which case they are called *mixed fertilizers*, or they may contain only one active ingredient, called *direct application fertilizers*. The advantage of using mixed fertilizers is that they contain all three primary nutrients—nitrogen, phosphorus, and potassium—and require a smaller number of applications. They can be liquids or solids. The overall percentage of the three nutrients must always be stated on the container. The grade designation is %N-%P<sub>2</sub>O<sub>5</sub>-%K<sub>2</sub>O and is commonly referred to as the *nitrogen-phosphorus-potassium (NPK) value*.

Phosphorus-based fertilizers usually are produced from wet-process phosphoric acid or directly from phosphate rock. Normal superphosphate, triple or concentrated superphosphate, and ammonium phosphate are the three common types used. Normal or ordinary superphosphate is mostly monocalcium phosphate and calcium sulfate. It is made from phosphate rock and sulfuric acid and is equated to a 20% phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) content. The production of normal superphosphate is similar to that for the manufacture of wet-process phosphoric acid except that there is only partial neutralization.

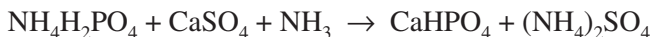
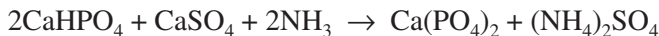
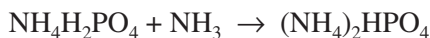
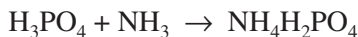


Triple superphosphate, made from phosphate rock and phosphoric acid, is mostly monocalcium and dicalcium phosphate.



Diammonium phosphate (DAP) is made from wet-process phosphoric acid of about 40% phosphorus pentoxide content and ammonia.

When an ammonia fertilizer is mixed with a superphosphate, a chemical reaction occurs that changes the active ingredient's structure.



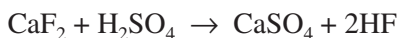
Slow-release or controlled-release fertilizers make application requirements less stringent. Urea-formaldehyde resins in combination with nitrogen fertilizers tie up the nitrogen for a longer time, whereas degradation of the polymer occurs slowly by sunlight. This type of fertilizer is especially popular for the high nitrogen content of home lawn fertilizers.

# FLUORINE

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Fluorine (melting point:  $-219.6^{\circ}\text{C}$ , boiling point:  $-188.4^{\circ}\text{C}$ ) is a pale greenish-yellow reactive gas that occurs in combined form in fluorine-containing minerals such as fluorspar, fluorapatite, and cryolite. Fluorine is also produced by the electrolysis of potassium bifluoride ( $\text{KHF}_2$  or  $\text{KF}\cdot\text{HF}$ ) under varying conditions of temperature and electrolyte composition.

Fluorspar is also used to manufacture hydrogen fluoride (hydrofluoric acid, aqueous and anhydrous) is manufactured in heated kilns by the reaction of fluorspar with sulfuric acid.



fluorspar

The hot, gaseous hydrogen fluoride is either absorbed in water or liquefied; refrigeration is employed to obtain the anhydrous product needed for fluorocarbon manufacture and other uses. Although hydrofluoric acid is corrosive, concentrations of 60% and above can be handled in steel at lower temperatures; lead, carbon, and special alloys are also used in the process equipment.

The largest production of fluorine compounds is that of hydrofluoric acid (anhydrous and aqueous), used in making *alkylate* for gasoline manufacture. It is also employed in the preparation of inorganic fluorides, elemental fluorine, and many organic fluorine- and non-fluorine-containing compounds. Aqueous hydrogen fluoride is used in the glass, metal, and petroleum industries and in the manufacture of many inorganic and acid fluorides. Three of the most unusual plastics known are Teflon, a polymerization product of tetrafluorethylene ( $\text{CF}_2=\text{CF}_2$ ).

Fluorine is also used for the manufacture of sulfur hexafluoride ( $\text{SF}_6$ ) for high-voltage insulation and for uranium hexafluoride. Fluorine is used directly or combined with higher metals (cobalt, silver, cerium, etc.) and halogens (chlorine and bromine) for organic fluorinations and the growing production of fluorocarbons.

Hydrogen fluoride is used to prepare fluorocarbons and one-third of the total goes to the aluminum industry, where synthetic cryolite, sodium aluminum fluoride, is a major constituent of the electrolyte. It is also consumed in the melting and refining of secondary aluminum. Other uses of hydrofluoric acid are found in the metals and petroleum industries.

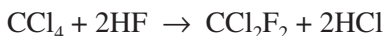
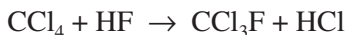
# FLUOROCARBONS

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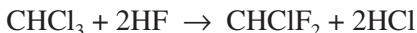
Fluorocarbons are compounds of carbon, fluorine, and chlorine with little or no hydrogen. Fluorocarbons containing two or more fluorine atoms on a carbon atom are characterized by extreme chemical inertness and stability. Their volatility and density are greater than those of the corresponding hydrocarbons. However, environmental regulations have restricted the use of many of these compounds.

Fluorocarbons are made from chlorinated hydrocarbons by reacting them with anhydrous hydrogen fluoride, using an antimony pentachloride ( $\text{SbCl}_5$ ) catalyst.

The fluorocarbons trichlorofluoromethane, dichlorodifluoromethane, and chlorodifluoromethane are major fluorocarbon compounds.



Difluoromono-chloromethane is made by substituting chloroform for the carbon tetrachloride.



In the process (Fig. 1), anhydrous hydrogen fluoride and carbon tetrachloride (or chloroform) are bubbled through molten antimony pentachloride catalyst in a steam-jacketed atmospheric pressure reactor at 65 to 95°C. The gaseous mixture of fluorocarbon and unreacted chlorocarbon is distilled to separate and recycle the chlorocarbon to the reaction. Waste hydrogen chloride is recycled by use of water absorption and the last traces of hydrogen chloride and chlorine are removed in a caustic scrubbing tower.

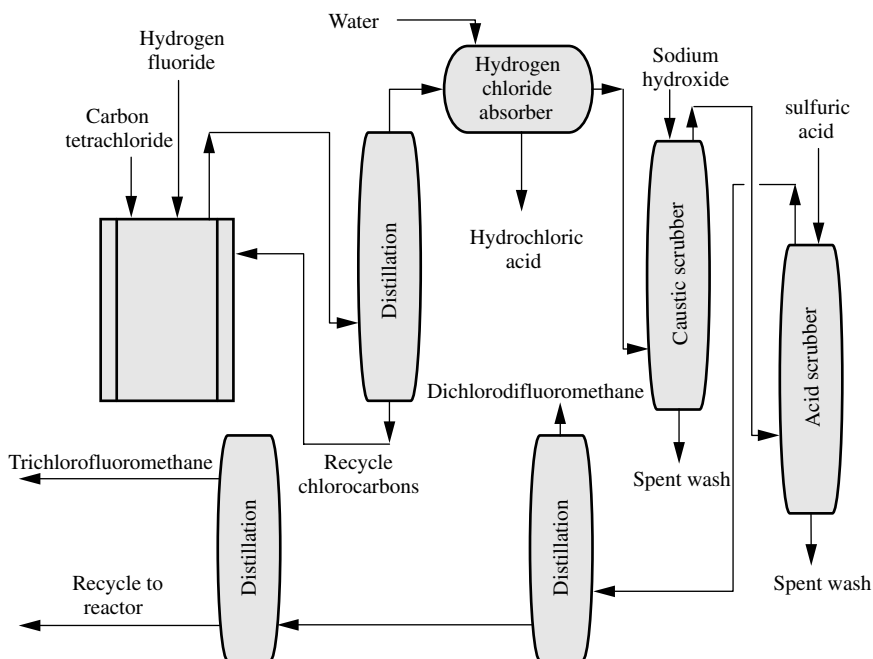
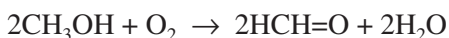


FIGURE 1 Fluorocarbon manufacture.

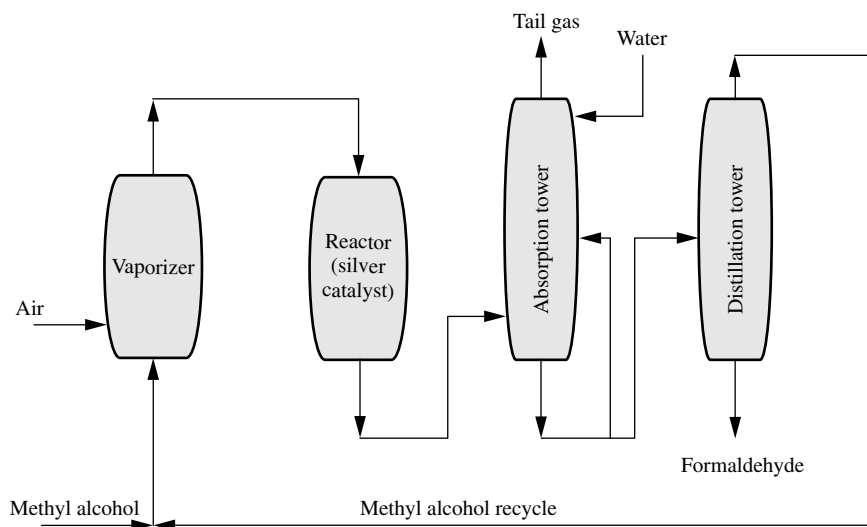
# FORMALDEHYDE

Formaldehyde (methanal, melting point:  $-92^{\circ}\text{C}$ , boiling point:  $-21^{\circ}\text{C}$ ) is produced solely from methanol by using a silver catalyst (Fig. 1) or a metal oxide catalyst (Fig. 2). Either process can be air oxidation or simple dehydrogenation.

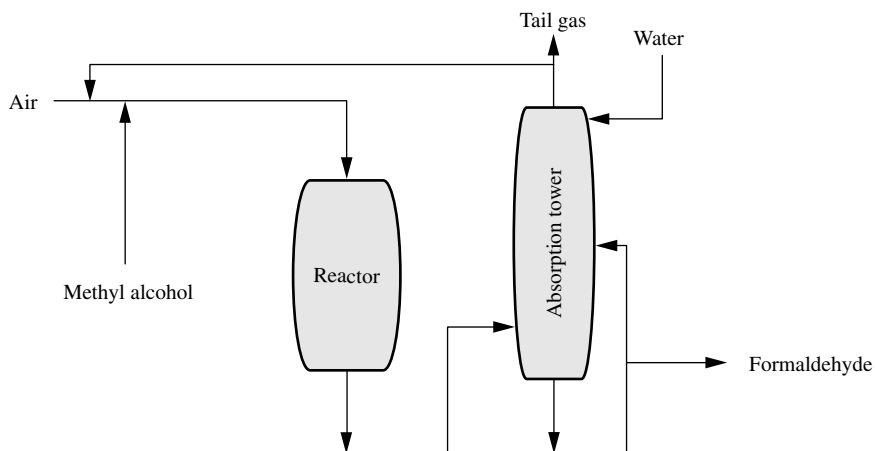


These two reactions occur simultaneously in commercial units in a balanced autothermal reaction because the oxidative reaction furnishes the heat to cause the dehydrogenation to take place.

In the process (Figs. 1 and 2), fresh and recycle methanol are vaporized, superheated, and passed into the methanol-air mixer. Atmospheric air is purified, compressed, and preheated to  $54^{\circ}\text{C}$  in a finned heat exchanger.



**FIGURE 1** Formaldehyde manufacture using a silver catalyst.



**FIGURE 2** Formaldehyde manufacture using a metal oxide catalyst.

The products leave the converter (a water-jacketed vessel containing the catalyst) at 620°C and at 34 to 69 kPa absolute. About 65 percent of the methanol is converted per pass. Temperatures are on the order of 450 to 900°C and there is a short contact time of 0.01 second.

The reactor effluent contains about 25% formaldehyde, which is absorbed with the excess methanol and piped to the make tank. The latter feeds the methanol column for separation of recycle methanol overhead, the bottom stream containing the formaldehyde and a few percent methanol. The water intake adjusts the formaldehyde to 37% strength (marketed as formalin). The catalyst is easily poisoned so stainless-steel equipment must be used to protect the catalyst from metal contamination.

In the pure form, formaldehyde in the pure form is a gas with a boiling point of -21°C but is unstable and readily trimerizes to trioxane or polymerizes to paraformaldehyde. Formaldehyde is stable only in water solution, commonly 37 to 56% formaldehyde by weight and often with methanol (3 to 15%) present as a stabilizer.

# FUROSEMIDE

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Furosemide, 4-chloro-*N*-furfuryl-5-sulfamoyl anthranilic acid, is prepared by treating 2,4,5-trichlorobenzoic acid with chlorosulfonic acid, and further treatment with ammonia and furfuryl amine.

Furosemide can also be synthesized starting with 2,4-dichlorobenzoic acid (formed by chlorination and oxidation of toluene). Reaction with chlorosulfonic acid is an electrophilic aromatic substitution via the species  $\text{-SO}_2\text{Cl}^+$  attacking ortho and para to the chlorines and meta to the carboxylate. Ammonolysis to the sulfonamide is followed by nucleophilic aromatic substitution of the less hindered chlorine by furfurylamine (obtained from furfural—a product obtained by the hydrolysis of carbohydrates).

Furosemide is used as a diuretic and blood pressure reducer.