thenes and aromatics (benzene) in the feed because, while these inhibit cracking, they also tend to retard paraffin isomerization. The presence of heptanes is undesirable as they crack readily and accelerate catalyst consumption. Aluminum chloride addition at a rate of 0.5 to 1.0 pound per barrel of feed is required to maintain catalyst activity.

The cost of light naphtha isomerization by this process is in the range of 0.7 to 1.0 cent per gallon reactor charge; this is stated to be competitive with the use of tetraethyllead for raising octane number, at current motor gasoline quality levels, only when very low octane feedstocks, consisting largely of normal paraffins, are available (*29*). However, in view of the upward trend in gasoline octane requirements, as well as the increasing cost of crude petroleum (which favors high yield processes such as isomerization), the economics of naphtha isomerization undoubtedly will become more favorable.

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NITRATION

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THE scope of this review covers nitration in its broadest sense—that is, the treatment of organic compounds with nitric acid or its equivalent to produce both nitrates and nitro compounds, as indicated by the following equations:

$$ROH + HO.NO_2 \rightarrow RO.NO_2 + HOH \qquad (1)$$

$$RH + HO.NO_2 \rightarrow R.NO_2 + HOH \qquad (2)$$
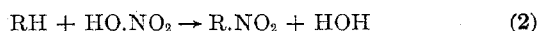
The nitration processes covered by this review deal with developments made and published since the start of World War II.

An over-all picture of the unit processes employed in nitration is presented, but no attempt is made to point out the merits of one process over the other, as this depends on individual requirements and the facilities available at the point of manufacture.

MANUFACTURE OF NITRIC ACID ESTERS

Nitration is the cornerstone of the explosive industry, which includes commercial blasting explosives, military explosives, and military and sporting smokeless powder. Nitration also plays an important role in the production of intermediates for the dye industry and of nitrocellulose for the protective coating and plastics fields.

The agent most commonly employed for nitration is mixed acid, a mixture of nitric and sulfuric acids with or without water, although nitric acid in varying degrees of concentration may be used alone. Groggins (*42*) gives a rather complete list of the agents used for nitration, depending on the procedure to be followed and the compounds to be nitrated. The mixture of nitric acid and acetic anhydride with or without acetic acid was used extensively during the war. Caesar (*16*) and Caesar and Goldfrank (*17*) describe a nitration process using nitrogen pentoxide (N₂O₅) with the addition of sodium fluoride for removal of by-product nitric acid, thus increasing the efficiency of the nitration. These authors also describe a method of preparing nitrogen pentoxide. Thomas, Anzilotti, and Hennion (*91*) state that many organic compounds nitrate quickly and almost completely with stoichiometric amounts of nitric acid when boron fluoride is added. According to these authors, the amount of boron fluoride required indicates that the reaction proceeds as follows:

$$R.H + HO.NO_2 + BF_3 \rightarrow R.NO_2 + BF_3.H.OH$$
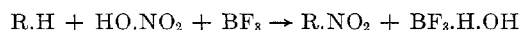
A procedure for recovery of boron fluoride is also described.

Recently there has been considerable interest in the use of acetic anhydride or a mixture of it and glacial acetic acid with nitric acid to effect nitration of certain alcohols and amines. Secondary and tertiary alcohols are difficult to nitrate with a nitric-sulfuric acid mixture. According to Lufkin (*65*), such alcohols may be readily nitrated by introducing a stream of the alcohol simultaneously with a separate stream of nitric acid into acetic anhydride to which 5 to 15% nitric acid has previously been added. Groggins (*42*) also mentions such mixtures.

In the explosives field sulfates reduce the stability of some

compounds and make them difficult to stabilize. The use of acetic anhydride as a dehydrating agent in the nitration process eliminates sulfate contamination, and in some instances this is of value, though more costly.

The batch process is used exclusively in the United States for the commercial nitration of glycerol, ethylene glycol, and the like. Although this procedure, described by Bennett (6), has been well standardized, a few changes have been made in materials of construction or method of fabrication—for example, the use of chrome steel alloys instead of lead for prewash tanks and the fabrication of nitrators by welding instead of riveting. All welded seams in such equipment are x-rayed to ensure homogeneity and freedom from pockets or cracks where nitroglycerin or other explosives might be deposited.

CONTINUOUS PROCESSES

In Europe, continuous processes are favored, as in some countries the size of the charge is limited by law. During World War II both batch and continuous processes were used in Germany for the manufacture of nitroglycerin, ethylene glycol dinitrate, diethylene glycol dinitrate, cyclotrimethylenetrinitramine, pentaerythritol tetranitrate, etc.

Of the continuous nitrators used for the manufacture of nitroglycerin, diethylene glycol dinitrate, and similar liquid explosives, the Schmidt-Meissner continuous nitrator, separator, and washing equipment are the best known and have been the subject of a number of patents taken out earlier in this country and abroad. Brooks et al. (12) describe the removal of Schmidt-Meissner continuous nitrators from the Benefeld Plant of Eibia, Bomlitz, Germany. Their report briefly describes the equipment and gives some operating and start-up data, including acid compositions for the nitration of diethylene glycol. Cooley (29) also discusses the manufacture of nitroglycerin and the like in Germany during the war, and gives a flow sheet of the Schmidt-Meissner equipment.

Other continuous equipment used in Germany included a Schmidt-Meissner continuous nitrator with a Biazzi separator and complete Biazzi plants, which include his nitrator, separator (8), and washing procedure. According to Ashcroft and colleagues (2), the Biazzi plant was installed at Schlebusch in 1938–39 and modifications were made up to 1940. These authors describe the Biazzi equipment, as well as a layout of a nitrating house using this equipment. The Biazzi separator which operates on a tangential principle, imparting a slight centrifugal action to the charge, is said to be more efficient than other continuous separators. A battery of these separators arranged in cascade has also been used to separate nitroglycerin from the wash waters. Ashcroft and colleagues have presented some operating data on the Biazzi plant, and state that a yield over a month period was 235% on a batch plant and 232% on the Biazzi unit, based on dry nitroglycerin produced from dry glycerol.

According to Biazzi, some European plants using the Schmidt-Meissner apparatus have installed his separator in the spent acid line after the Schmidt unit to clean up the spent acid, thus reducing "after" separation at the spent acid storage.

To date there is no record in the literature searched covering the Biazzi continuous nitrator.

Öhman (73) investigated the reaction equilibria in conjunction with the nitration of diethylene glycol. His article also gives references to earlier work of a similar nature pertaining to the nitration of glycerol and ethylene glycol.

Continuous apparatus for the nitration of solid materials and the production of solid nitrated compounds have also been devised and used commercially in European countries; whereas, to date, the batch process has been preferred in this country in most cases.

The Germans used a continuous unit for the manufacture of pentaerythritol tetranitrate. Stickland and colleagues (87) describe this procedure and give the amount of materials required

in practice to produce 100 units of pentaerythritol tetranitrate, based on the nitration of pentaerythritol with 99% nitric acid according to the following equation,

$$C(CH_2OH)_4 + 4HNO_3 \rightarrow C(CH_2ONO_2)_4 + 4H_2O$$
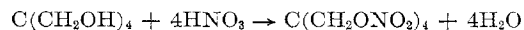
as 44.4 of pentaerythritol and 224 of nitric acid with a loss of 16 units of nitric acid. No data are given on acetone consumption for purification. Cooley (29) also describes the German process, giving a flow sheet of the plant. Swanson (89) gives a detailed description of the nitrating and purification procedure for the manufacture of pentaerythritol tetranitrate in Germany, including quantities of materials charged into the system and time cycles. He points out that at one time the purification procedure was a continuous process, but a better solution of the pentaerythritol tetranitrate in acetone was obtained batchwise. Hence, two dissolving kettles were installed, which were charged and discharged alternately, so that a continuous feed of solution was maintained to the crystallizer and continuous acetone recovery system.

A continuous nitrator for the manufacture of pentaerythritol tetranitrate is described by Crater (31). Acken and colleagues (1) describe the nitration of pentaerythritol at temperatures above 100° F.

NITROCELLULOSE

Cellulose nitrate (nitrocellulose) plays an important role in the explosives industry, both in commercial blasting explosives and in smokeless powder used for sporting and military purposes, and large quantities are used by the protective coating industry and for the manufacture of plastics.

Formerly the chief source of cellulose for nitration was cotton linters. Today cellulose, obtained from wood and known to the trade as wood cellulose, has virtually replaced cotton linters for the manufacture of most grades of nitrocellulose.

Thoenges (90) lists the various grades of nitrocellulose and their uses, describes the nitration of cellulose, and includes a flow sheet of a process. Barsha (3) also describes the manufacture of nitrocellulose, gives acid compositions, rates of reaction, and properties of the various grades produced, and discusses the mechanism of cellulose nitration. Other work on the nitration of cellulose was carried out by Wilson and Miles (96). Desmaroux and co-workers (34) investigated the nitration of cellulose in mixtures of nitric acid and oxygen-containing materials. Chédin and colleagues (22–24) have published a number of articles on the mechanism of nitration of cellulose. Sheldon (84) discusses the various types of wood cellulose used in Germany for the manufacture of nitrocellulose during World War II and covers the German process for nitration of cellulose, giving acid compositions and ratios of acid to cellulose. He points out that wringer fires or fume-offs were rare, possibly because of the arrangement of the nitrator discharge pipe carrying the spent acid–nitrocellulose slurry to the centrifuge. The swing portion of this pipe is actuated by the opening and closing of the discharge valves of the nitrator, so that when this valve is opened the pipe is in position to deliver the charge into the centrifuge basket. When the valve is closed, the end of the discharge pipe is outside the basket, and it is thus impossible for drops of acid to drip into the basket during the wringing.

Stickland et al. (87) describe the manufacture of nitrocellulose at the Krümmel Plant of Dynamit A. G., Germany, and give plant capacities together with equipment data and operating procedure covering nitration and stabilization. Acid compositions for nitrocellulose containing 11.25 to 11.50% and also 13.2 to 13.3% nitrogen are, respectively, 16 to 18% water, 20% nitric acid, and 64 to 62%, sulfuric acid; and 9 to 10% water, 22.5% nitric acid, and 68.5 to 67.5% sulfuric acid.

Processes for the continuous nitration of cellulose have been patented, but to date have not been adopted on a commercial scale. Berl (7) has taken out a patent covering the continuous

production and stabilization of nitrocellulose and other compounds as nitrostarch. His nitrating mixture comprises water-free nitric acid, water-free phosphoric acid, and phosphoric acid anhydride, or a mixture of water-free nitric acid, water-free acetic acid, and acetic anhydride. The use of these dehydrating agents compared with sulfuric acid adds considerably to the acid cost. Caesar (15) covers the nitration of cellulose and starch with a mixture of nitrogen pentoxide dissolved in chloroform in the presence of phosphorus pentoxide. He claims a batch and a continuous process. According to the examples cited, high-nitrogen material is readily produced and stabilized, but here again the cost of the nitrating and dehydrating agent would be high.

Other patents on the process of manufacturing nitrocellulose include that of Bouchard et al. (9), who patented a process for separating the nitrocellulose from the spent acid so that denitration of the nitrocellulose is reduced to a minimum. McKee (66) describes a new style nitrator for the manufacture of nitrocellulose, using mixed acids of various strengths which are removed by displacement, the final acid being displaced with water.

Jahn and Coppick (57), who recently patented the nitration of lignocellulose, state that the nitrated product is of interest in the manufacture of clear films and plastics. Friese (39) describes a process for the nitration of wood or straw, which is added to a mixture of acetic anhydride and glacial acetic acid with the slow addition of nitric acid (density, 1.52). Schur (83) covers the method of preparing wood cellulose for nitration, in which a sheet of felted wood pulp is formed and then clipped to give suitable particles having a length less than the thickness of the original sheet.

According to Walter and colleagues (92), in a novel continuous process used by the Germans for the manufacture of methyl nitrate methanol reacted with 60% nitric acid in a fractionating plate column. By proper control of the operation, varying concentrations in the methanol of methyl nitrate ranging from 60% to 100% may be produced. Methyl nitrate made by this process is said to be chemically pure, and to require no additional stabilization. The plant is claimed to have operated for a year without accident. A flow sheet of the apparatus is included in the report. In most cases the methyl nitrate was used in admixture with methanol, a 75-25 mixture being preferred, as according to some reports (74) pure methyl nitrate is very dangerous to handle. This latter report also discusses the manufacture of methyl nitrate.

MANUFACTURE OF NITRO COMPOUNDS

The foregoing processes of nitration cover the manufacture of nitric acid esters in accordance with Equation 1. The following processes cover procedures for the manufacture of true nitro compounds as indicated by Equation 2. The nitrated aromatic hydrocarbons form an important group, which includes trinitrotoluene, the most widely used military high explosive, as well as the nitrobenzenes and various nitroaromatics used as intermediates in the dye industry and for other purposes as the preparation of amines. Thus, these processes of nitration are of interest not only to the explosives industry but to a number of other industries as well.

NITRATION OF TOLUENE

Generally, the nitration of toluene to the tri-stage is carried out in three steps for economical reasons, although in some processes it is nitrated to the bi- stage and then to the tri- stage. In the United States large quantities of trinitrotoluene were manufactured during the past war by a batch process that consisted of three stages of nitration—toluene to mononitrotoluene, mononitrotoluene to binitrotoluene, and binitrotoluene to trinitrotoluene. These three stages are commonly termed mononitration, binitration, and trinitration.

A mixture of nitric and sulfuric acids is used to effect nitration, the composition varying with the stage of nitration.

The mixed acid used for the mononitration contains approximately 48% sulfuric acid, 18% nitric acid, 14% nitrosylsulfuric acid, 8% nitrotoluenes, and 12% water. It is prepared by fortifying the spent acid from the binitration with nitric acid. Part of the mono- spent acid, termed cycle acid, is placed in the nitrator first, the toluene is added to it, and then the mixed acid is added. The role of cycle acid is to reduce the violence of the reaction.

After the nitration is complete, the mononitrotoluene is separated from the acid and sent to the binitrator. Part of the mono- spent acid is retained for cycle acid, and the remainder is sent to the acid recovery, where it is passed through a denitrating tower to recover the nitric and sulfuric acids which are reconcentrated for subsequent use.

The spent acid from the trinitration is fortified with nitric acid and used for binitration. The composition of this acid is approximately 50% sulfuric acid, 20% nitric acid, 12% nitrosylsulfuric acid, 12% nitrotoluenes, and 6% water.

New acid used for the trinitration consists of 30 to 40% oleum, which is first added to the "bi-oil"; then semimixed acid containing about 40% sulfuric acid and 60% nitric acid is added.

Thus, the original sulfuric acid is used three times, and the process of nitration is in reality a three-stage countercurrent process involving the toluene and the acid. The amount of sulfuric acid in the process remains the same in the three nitrations; on the other hand, the amount of water increases as the charge of acid passes from the trinitration to the mononitration. The amount of nitric acid varies, part of it being used in each nitration, and more is added to make up the desired concentration for the next lower nitration.

The acid trinitrotoluene obtained from the trinitration is sent to the wash house, where it is washed, stabilized, and flaked or grained. The stabilization procedure varies with the grade of material being produced.

Clift and Fedoroff (27) discuss in detail the manufacture of trinitrotoluene, its properties, and analyses, and give a flow sheet of a three-stage process together with data on acid compositions and acid calculations.

The Germans also manufactured trinitrotoluene by a three-stage nitration process described by Stickland et al. (87). Acid compositions, time cycles, and washing procedure are included in this discussion. One point of difference between the American process and the German process is that the Germans neutralized and purified the mononitrotoluene before subsequent nitration. The use of impure toluene made this extra step necessary.

According to Stickland et al. (88), some mononitrotoluene was also manufactured in Germany by the D.A.G. (Dynamit Aktien Gesellschaft) continuous process, which is stated to be superior to Meissner's. No description of the D.A.G. process is available in the open literature.

In Meissner's continuous process (71) the nitrating acid is introduced in the bottom of the nitrator and the material to be nitrated is added at the top of the vessel. The material to be nitrated enters a central tube equipped with an agitator exerting a downward thrust, which forces the material down through the acid and up through a series of tubes, set in tube sheets and surrounded by a cooling medium. The nitrated product and spent acid are discharged from an overflow located near the top of the vessel.

Stickland et al. (88) state that the Germans worked on the vapor-phase nitration of toluene direct to trinitrotoluene but give no data on this process.

Papazoni (77) patented a process for the manufacture of trinitrotoluene in which the acids used for the mono- and binitration stages were fortified in the nitrator, rather than in separate vessels. By this procedure the fortifying tanks and blowcases are eliminated, and the hazard of the manufacture of trinitrotoluene is reduced; these blow cases in the past have been a source of a number of explosions. Papazoni adds the toluene and mononitrotoluene directly to the mixed acid, which is the reverse of the practice formerly followed.

Castner (21) describes a nitration process, which is applicable to the nitration of organic materials where a number of nitration

stages are possible and where it is desired to avoid overnitration. The process is suited to the nitration of toluene, benzene, xylene, chlorobenzene, mononitrotoluene, and the like. In the method described by Castner, separate layers of the nitrating acid and the organic material are obtained in a liquid state capable of nitration, and contact between two liquids at the interface is maintained by providing separate agitation for each layer.

According to McKee (67), lower nitrated derivatives may be separated from higher nitrated derivatives of nitrated compounds having a single benzene ring by treating such mixtures with an aqueous solution of a readily soluble salt of a mononuclear acid of the benzene series. This process is particularly adapted to the removal of the lower nitrated derivatives from crude trinitrotoluene and on subsequent dilution of the solvent with water, the lower nitrated derivatives may be recovered. This procedure is also applicable to the purification of trinitrobenzene and tetryl.

Mono- and binitrotoluenes may be produced by nitrating toluene with nitric acid alone, as described by Crater (30). Such a process is of advantage when the lower nitrated derivatives are required, as the use of sulfuric acid is eliminated, and the acid recovery problem is thus made easier. Othmer and Kleinhans (76), studying the production of mononitrotoluenes from toluene and nitric acid alone, used a partial pressure process, and investigated reaction velocities, acid concentrations, and acid ratios. According to these investigators, the continuous process gives higher yields and lower costs than the process using mixed acid. Equipment costs may be higher per unit, owing to type of materials used for fabrication, but the complete plant may cost less, as certain units are eliminated.

To produce a mononitrotoluene rich in p-nitrotoluene, Wright and Donaldson (98) prepared an admixture of toluene and a nitric ester of a monohydroxy alcohol containing from two to five carbon atoms, then added sulfuric acid while keeping the temperature not lower than 40° C. Specifically, toluene and ethyl nitrate are mixed together and treated with 98% sulfuric acid at a temperature not exceeding 60° C., followed by the addition of more ethyl nitrate. The charge is cooled and diluted with water, and the aqueous acid layer is separated from the mononitrotoluene isomers, which are neutralized and then distilled under reduced pressure for separation.

I. G. Farbenindustrie (56) worked out a process of nitration in which the substance to be nitrated is added in the form of a mist instead of the gas phase. Whereas the gas-phase process is restricted to relatively volatile substances, by the mist process, substances having a very low vapor pressure can be put into a mist form. Even solids may be nitrated by dissolving them in an inert solvent and putting this solution into a mist. The nitration of mononitrotoluene by this process is given as an example, and a multistage process for its nitration is mentioned.

OTHER AROMATIC COMPOUNDS

The foregoing nitration procedures for the nitration of aromatic compounds deal primarily with the nitration of toluene, although some of these procedures when modified are applicable to the nitration of compounds like benzene and xylene. Nitration processes applicable to the manufacture of other nitroaromatic compounds, which are of interest to the dye and other industries, are discussed below.

The nitration of benzene to various stages, using a mixture of sulfuric and nitric acids, is described in detail by Groggins (42), who gives operating data, including time cycles, yields, and acid compositions. Another process for the nitration of benzene, described by Mares (69), comprises the addition of aqueous nitric acid to a mixture of benzene, sulfuric acid, and water under such conditions of temperature and pressure that the water present in nitric acid and that formed by the reaction are removed by distillation of the azeotropic benzene-water mixture. The benzene-water distillate is condensed, and the components are separated

from each other. The amounts of water added with the nitric acid plus the water of reaction are discarded, and the remainder of all water plus all the benzene is returned to the reactor, thus maintaining constant the predetermined ratio of sulfuric acid to water in the reactor. By following such a procedure, the reaction is carried out in the presence of sulfuric acid having a constant dehydrating value, which if properly established should give an optimum nitrating condition. This process can be operated either as a batch or continuous process. Its advantage is the elimination of spent acid and the subsequent recovery of such acid. Castner (20) also patented a process similar to that of Mares.

In Kokatnur's (59, 60) process for the nitration of aromatic compounds with nitric acid, the water of reaction is removed by the formation of an azeotrope with the material being nitrated or an added solvent capable of forming an azeotrope with water but inert to the nitrating acid. Among the compounds listed by Kokatnur as produced by his process are nitrobenzene, nitronaphthalene, m-dinitrobenzene, and trinitrotoluene.

Othmer and co-workers (75) investigated the nitration of benzene with nitric acid alone and the removal of the water of reaction by distilling off the azeotropic mixture of water and benzene. Considerable nitric acid was carried off by entrainment, but this entrainment was substantially reduced by installing a suitable column and separator. The authors designed a plant for the continuous production of nitrobenzene and present a flow sheet showing the plant process and equipment. The plant process uses vapor feed instead of liquid feed of the nitric acid, as it was found to increase the conversion materially.

A process for the vapor-phase nitration of aromatic hydrocarbons to their mononitro derivatives, using nitric acid or nitrogen dioxide in the presence of a catalyst, was patented by Rout (79). Suitable catalysts are metallic metaphosphates, boron phosphate, or a calcined mixture of pyrophosphoric acid and a solid absorbent. About 27% conversion of benzene to nitrobenzene takes place when benzene is vaporized at the rate of 200 ml. per hour, mixed with 98% nitric acid vaporized at the rate of 35 ml. per hour, and passed over calcium metaphosphate. The vapor-phase nitration of toluene was studied by Bullock and Mitchell (14), who report yields varying from 30 up to 62%, depending on conditions.

The process of nitrating aromatic carbocyclic compounds, using a nitrating mixture made up of nitric acid, boron trifluoride, and the compound to be nitrated and maintaining the mixture at such a temperature that nitration is effected, was patented by Hennion (49). Examples for the nitration of nitrobenzene, p-toluenesulfonic acid, toluene, benzene, benzoic acid, methyl benzoate, phthalic anhydride, etc., are given. Thomas, Anzilotti, and Hennion (91) discuss the effectiveness of boron fluoride as a dehydrating agent for sulfonation and nitration reactions. According to them, many organic compounds nitrate quickly and almost completely with stoichiometric amounts of nitric acid in the presence of boron fluoride. The amount of boron fluoride required indicates that the reaction proceeds as follows:

$$R-H + HNO_3 \rightarrow R-NO_2 + BF_3.H_2O$$
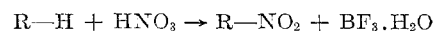
The process of nitrating benzene and organic compounds in a film reactor has been investigated. Dahmen (32) reports yields of up to 89% nitrobenzene and 4% dinitrobenzene, and that temperature changes between 40° and 85° C. had little effect. Patents covering the nitration of organic compounds in film reactors have been granted to Waterman et al. (93) and N. V. de Bataafsche Petroleum Maatschappij (72). In both cases the material to be nitrated is allowed to flow in a thin layer over a surface, which may be cooled or heated, and then the nitrating acid is introduced. Waterman et al. spray the acid, whereas in the latter case it is distributed by a rotating slinger.

Dolt and Hill (35) describe a procedure for making dinitrocresol, in which a cresol sulfonation mixture, formed by mixing a cresol and concentrated sulfuric acid, is added directly to dilute

nitric acid at room temperature. Then the temperature is allowed to rise to 40° C., and the mixture is subsequently heated to about 80° to 100° C.; finally the dinitrocresol is separated. The addition of the sulfonated cresol to the nitric acid is similar to the direct nitration procedure of toluene and mononitrotoluene described by Papazoni (77) and is the reverse of the practice commonly followed heretofore.

Britton and Dosser (11) describe a process for the nitration of o-cyclohexylphenol to produce 2, 4-dinitro-6-cyclohexylphenol. The process comprises sulfonation and subsequent nitration by the addition of a solution of ammonium nitrate.

Galloway (40) has patented a process for the nitration of 4-tertiary alkylphenols such as 4-tert-amylphenol for the production of their nitro derivatives, which according to the patent are used for making amines useful as gasoline antioxidants.

Mechanism and Kinetics. Several investigators have studied the mechanism and the kinetics of the nitration of aromatic compounds. Bennett and co-workers (4, 5) studied rates of nitration and the active nitrating agent. The kinetics of the nitration of aromatic nitro compounds were investigated by Westheimer and Kharasch (94), who studied rates of reaction and the active nitrating agent. A series of articles in Nature (41, 44, 54) discusses the mechanism of nitration of aromatic compounds using sulfuric-nitric acid mixtures. McKinley and White (68) investigated the rate of nitration of toluene using mixed acid, and Lewis and Suen (64) studied the effects of variables on the nitration of benzene with mixed acid in both continuous and batch processes. The mechanism of the oxynitration of benzene was investigated by Westheimer et al. (95) for the production of picric acid.

Tetranitromethane was investigated by the Germans as an oxygen donator in place of nitric acid for use in the V weapons. Hunter (55) investigated the manufacture of tetranitromethane in Germany; according to his report, Schimmelschmidt is credited with working out a process of reacting acetylene with nitric acid for its production based on the early work of the English chemists, Orton and McKee. The reaction is believed to proceed in a number of stages; about 60% of the acetylene reacts to give tetranitromethane and about 40% is completely oxidized. The over-all reaction can be represented by the following equation:

$$5C_2H_2 + 38HNO_3 \rightarrow 3(NO_2)_4C + 24H_2O + 7CO_2 + 26NO_2$$
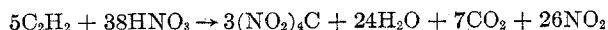
To promote the reaction, mercury as the nitrate was used as a catalyst. The report cited describes a large-scale laboratory apparatus for the nitration of acetylene to produce tetranitromethane; a flow diagram of the process is included. The setup is complete, including pumps, a nitric acid concentrating column, and a sulfuric acid concentrator. The mercury is recovered as mercuric sulfate and reconverted to the nitrate for subsequent re-use. Nitroform, $CH(NO_2)_3$, is formed in the process as an intermediate, and may be extracted in a pure state at 0° C. by using nitrogen dioxide as a solvent.

NITROPARAFFINS

In recent years there has been considerable interest in the production of nitroparaffins. Generally alkane hydrocarbons resist direct nitration; however, improved methods of nitration at high temperatures and pressures have made a number of nitroparaffins commercially available at lower costs. The nitroparaffins are useful solvents for a number of organic compounds, including cellulose esters, resins, oils, fats, and waxes. Various derivatives of this series of compounds as their condensation products with aldehydes have commercial application; their amines formed by reduction are useful as emulsifying agents, while the chloronitroparaffins are active insecticides. Levy and Rose (63) have recently reviewed the field of the nitroparaffins, covering developments of the last few years. They discuss a number of nitration reactions and reactions of the nitrated product with various other compounds and list the uses of nitroparaffins. An earlier review by Hass and Riley (47), which includes over 400 literature references, deals with the liquid- and vapor-phase nitration of saturated hydrocarbons and also miscellaneous methods of introducing the nitro group by the oxidation of a primary amine direct to a nitroparaffin. The properties, toxicity, uses, and reactions of the nitroparaffins are discussed and outlined.

The development of direct nitration procedures for the nitration of the paraffin hydrocarbons was largely due to efforts of H. B. Hass and his colleagues, who have taken out a number of patents and published several journal articles on the subject. Groggins (42) discusses the nitration of the paraffin hydrocarbons and gives flow diagrams of equipment, operating data, and cost figures.

Hibshman, Pierson, and Hass (50) describe the vapor-phase nitration of ethane, which gives a mixture of nitromethane and nitroethane in the ratio of about 27 to 73 by weight. Optimum operating conditions are a temperature of 455° C. with a mole ratio of ethylene to nitric acid of 10 to 1 at a pressure of 100 pounds per square inch and a contact time of 0.33 second. Stainless steel apparatus was used. Potassium nitrate was added to the nitric acid to mask the catalytic effect of the stainless steel walls on the oxidation reaction, and a reaction chamber was designed to study the variation of conditions. It is apparent that ethane is not a suitable source of nitromethane, unless a large market for nitroethane exists. In a subsequent article by Boyd and Hass (10) the nitration of methane is discussed. The production of nitromethane is brought about by the direct reaction of commingled streams of methane and nitric acid in carbon dioxide and steam at a temperature of about 475° C. Pure methane was obtained from natural gas, and this process is also described.

Grundmann (43) studied the nitration of the paraffin hydrocarbons of higher molecular weight and gives diagrams of the apparatus. He states that nitration difficulties of reported methods can be overcome by passing finely dispersed superheated nitric acid vapor through the liquid hydrocarbons, which have been preheated to the reaction temperature. The process is considered to be without danger when alkanes containing eight or more carbon atoms are nitrated. The reaction and separation of the reaction products are discussed.

Danzig and Hass (33) discuss the nitration of 2,3-dimethylbutane, and Howe and Hass (53) treat the nitration of neopentane and neohexane, including operating data and the products obtained.

Hass and Hodge (46) patented a process for the nitration of saturated hydrocarbons of the paraffin series having more than two carbon atoms, by contacting wholly in the vapor phase and chemically combining such hydrocarbons and nitrogen dioxide at a temperature of 300° to 600° C. This process may be operated continuously. A flow diagram of the apparatus is included with examples and operating data.

Johnson (58) describes a cyclic process for the nitration of the lower alkanes using nitric acid vapor or nitrogen dioxide as the nitrating medium. The unreacted alkane remaining in the gaseous reaction products is recovered and recycled in the process, and the gaseous reaction products including the lower nitroalkanes, aldehydes, and ketones are separated.

In the vapor-phase nitration of hydrocarbons, after a time, yield and conversions drop off under continued operation of the equipment. When this occurs, the reaction vessel is described as "deactivated." The occurrence is similar in nature to the poisoning of a catalyst used in catalytic reactions. Martin (70) patented a procedure for inhibiting the deactivation of apparatus used for the nitration of hydrocarbons by the vapor-phase process by means of a molten salt bath for vaporizing nitric acid used in the nitration process. The salts preferably used for the bath are the nitric acid salts of alkali and alkaline earth metal compounds that are stable in the presence of nitric acid. Several of these salts are listed in the patent, and an example illustrating the process is given. Landon (61) overcame deactivation by constructing the reaction vessel from materials having substantially

no negative catalytic effect—glass, fused silica, gold, or platinum—or using vessels lined with these materials. A diagram of equipment suitable for conducting such a nitration is included, together with a description of the process.

Rideout (78) describes a process for the vapor-phase nitration of methane, whereby an inert gas, such as nitrogen, is added to the gaseous reactants of methane and nitric acid, effecting an increase in the yield of nitromethane. A diagram of the apparatus and yield data are included and the method of carrying out nitrations by this process is described.

Hodge (51) describes the procedure of controlling the acidity of the aqueous layer within the range 0.1 to 1.5 normality in order to obtain maximum conversion to nitroalkanes when nitrating alkanes contain two or more carbon atoms. Either nitric acid or nitrogen dioxide may be used to effect nitration. Four examples are included.

The liquid-phase nitration by means of nitric acid of saturated hydrocarbons, such as the paraffins and cycloparaffins, according to Sankus (81), is accomplished by using a catalyst that reduces nitric acid under the conditions of nitration. Catalytic materials used by Sankus are sulfur, decolorizing carbon, nitric oxide, methyl alcohol, acetone, and the nitrated products themselves. The reaction is carried out over the temperature range of 125° to 150° C. with agitation. Several examples are cited.

A catalyst is used by Levy (62) to promote the reaction between nitric acid and a paraffin hydrocarbon. A mixture of the hydrocarbon to be nitrated and nitric acid, both heated to a gaseous state, is passed through a chamber packed with fragments of borosilicate glass containing compounds of arsenic and antimony at a temperature between 300° and 450° C.

Stengel and Egly (86) patented a continuous process for the vapor-phase nitration of alkanes, which are preheated to a predetermined temperature and passed into an elongated reactor, where liquid nitric acid is introduced at various points in a finely divided state into the preheated alkane, so that the desired temperature of nitration is maintained. The nitrating apparatus is described and the reaction procedure discussed. Examples describing the operation are also given.

Hass and his colleagues and other investigators have studied the mechanism of nitration of alkanes. The vapor-phase nitration of aliphatic hydrocarbons was investigated by Hass and Shechter (48), who make thirteen generalizations concerning these reactions. Egloff and co-workers (37) discuss in detail some of the uses and methods of nitrating alkanes, alkenes, and alkynes by nitric acid vapor, nitrogen oxides, and electrochemical processes, giving fifty-seven references. Hass (45) reviewed recent work on the mechanism of vapor-phase nitration of paraffin hydrocarbons.

Another interesting series of nitro compounds is the nitroamines, some of which are powerful and stable explosives. Probably the one of greatest interest during World War II was "cyclonite" (cyclotrimethylenetrinitramine). Germany and the Allies produced and used large quantities of this explosive, which was generally used in admixture with other components.

MANUFACTURE OF CYCLONITE

According to Cooley (29), five methods of manufacturing cyclonite were used in Germany. These processes are described in detail by Stickland and his team (87), who surveyed German explosive plants, and by Brooks and colleagues (13), who also included flow sheets and photographs of some of the equipment. A report prepared by Sager and Swanson (80) describes the manufacture of cyclonite in Germany, and gives flow sheets.

W Process. This process, named after Wolfram of I. G. Farbenindustrie, is made up of a series of six reactions, the sixth of which is the nitration of potassium methyleneaminosulfonate to give cyclonite. This reaction may be represented by the following equation:

$$3CH_2\!\!=\!\!NSO_2OK + 3HNO_3 \rightarrow (CH_2NNO_2)_3 + 3KHSO_4$$
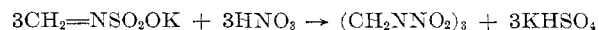
Under operating conditions used, about an 80% yield of cyclonite based on the formaldehyde used is claimed.

E Process. This process was developed by Ebele, and cyclonite was manufactured by it at the Bobingen plant of Dynamit A. G. The process consists of the simultaneous addition of paraformaldehyde, ammonium nitrate, and acetic anhydride to the reaction vessel in such a manner that the temperature of reaction is controlled within the desired range. The reaction may be represented by the following equation:

$$3HCHO + 3NH_4NO_3 + 6(CH_3CO)_2O \rightarrow \\ (CH_2NNO_2)_3 + 12CH_3COOH$$
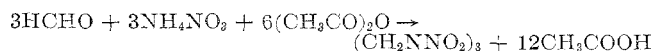
This process was said to give about a 60% yield of cyclonite based on the formaldehyde used.

K Process. This procedure was worked out by Knoffler, who proceeded on the basis that hexamethylenetetramine contains six CH_2 groups and four NH_2 groups; hence he proposed using a reaction mixture containing ammonium nitrate in addition to hexamethylenetetramine and concentrated nitric acid. However, only a small unit was installed for making cyclonite by this process, because the K and E Processes were combined (see KA Process below). The working up of the spent acids from K Process gave considerable difficulty. The K Process reaction may be represented by the following equation:

$$C_6H_{12}N_4 + 2NH_4NO_3 + 4HNO_3 \rightarrow 2(CH_2NNO_2)_3 + 6H_2O$$
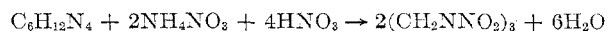
Based on formaldehyde used, the yield of cyclonite was about 65%.

SH Process. This process was developed to large-scale production by Schnurr, using the ideas of Henning's patent of 1899, which comprises the direct nitration of hexamethylenetetramine with concentrated nitric acid to produce cyclonite. Only about 40% of the formaldehyde and 60% of the nitrogen react to give cyclonite, and the remainder is left dissolved in nitric acid. After a time the part dissolved in the acid is oxidized to carbon dioxide, with the formation of large amounts of nitrous oxide and the evolution of considerable heat, which may lead to the explosion of the cyclonite produced. Schnurr achieved stabilization of the spent acid by introducing a controlled "cook-off" step immediately after the nitration process. Yields of about 70% based on formaldehyde used were said to be attained, and the reaction may be represented by the following equation:

$$C_6H_{12}N_4 + 6HNO_3 \rightarrow (CH_2NNO_2)_3 + 6H_2O + 3CO_2 + 2N_2$$

KA Process. The KA Process is a combination of the K and E Processes. Its advantage over the E Process is the use of hexamethylenetetramine dinitrate in place of formaldehyde, because the same yield of cyclonite produces only half as much water, and thus requires only half the amount of acetic anhydride. According to reports, about an 80% yield based on formaldehyde used was obtained by the KA Process, the reaction of which may be represented by the following equation:

$$C_6H_{12}N_4 \cdot 2HNO_3 + 2NH_4NO_3 \cdot HNO_3 + 6(CH_3CO)_2O \rightarrow \\ 2(CH_2NNO_2)_3 + 12CH_3COOH$$
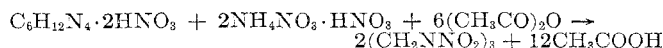
A patent recently granted to Schiessler and Ross (82) covers the preparation of cyclonite by the reaction of formaldehyde with ammonium nitrate in the presence of acetic anhydride. The process described by Schiessler and Ross corresponds to the German E Process. Wright et al. (97) describe a process for the nitration of hexamethylenetetramine based on the Bachmann process (patent not yet issued), which consists of reaction of this material with nitric acid and ammonium nitrate in the presence of acetic anhydride. The process described by Wright et al. is similar to the German KA Process, and the same over-all equation is representative of both processes. The one point of difference is that Wright et al. dissolve the hexamethylenetetramine in glacial acetic acid and react this solution; whereas in the KA Process hexamethylenetetramine reacts first with 50% nitric acid to give the dinitrate, which is added in a dry state to a reaction mixture of nitric acid and ammonium nitrate.

According to Connor (28), large quantities of cyclonite were manufactured in the United States during World War II by the modified Bachmann process and by direct nitration of hexamethylenetetramine.

Chute and his co-workers (26) describe a process for the nitration of diethanolamine for the production of β,β-dinitroxydiethylnitramine (Dina). The crux in this nitration process is the use of hydrogen chloride or one of its salts as a catalyst. Nitration is effected by using nitric acid in acetic anhydride, and the molar ratios of diethanolamine–nitric acid–acetic anhydride–diethanolamine hydrochloride are 1 to 3.2 to 3.4 to 0.05.

Dunn and colleagues (36) found that amines that do not require a chloride catalyst for their nitration are more weakly proton accepting than amines that cannot be nitrated without catalyst. They also found that such weak proton-accepting amines, which can be nitrated without catalyst, are further typified by their tendency to coordinate with themselves in about 16% association in acetic acid solution; whereas amines that cannot be nitrated without a catalyst are not associated in this medium. A series of secondary amines, on which the proton-attracting ability had been previously determined, was nitrated by Chute and co-workers (25), who found the gradation in ease of nitration to vary inversely with the proton-attracting ability of the amine. Chromatographic analysis was also made of some of the nitrated amines.

Wyler (99) describes a process for the manufacture of cyclonite, whereby hexamethylenetetramine reacts with nitric acid in the presence of phosphorus pentoxide. This process is stated to give yields up to 90% of theory. Wyler (100) also patented a process comprising the reaction of hexamethylenetetramine with nitric acid containing an ammonium salt selected from the group containing ammonium nitrate and ammonium sulfate, where the amount of ammonium salt was not more than the equivalent of about 1 part of ammonia per 50 parts of 100% nitric acid.

Another process for the nitration of amines, patented by Caesar and Goldfrank (18), is specific to nitration of hexamethylenetetramine, which reacts with nitrogen pentoxide dissolved in a nonaqueous solvent, such as chloroform, carbon tetrachloride, and propylene dichloride. The process may be operated batchwise or continuously, and high yields of the nitrated product are said to be obtained. When nitrogen pentoxide is used, no water is liberated but some formaldehyde is liberated as a by-product, but this apparently is not oxidized as is the case when nitric acid is used. Another patent (19) issued to these same inventors describes the nitration of ethyleneurea to give its dinitro derivative by a similar process. However, when ethyleneurea is nitrated with nitrogen pentoxide, some nitric acid is liberated, and this may be removed from the nitrating solution by using a fluoride salt (16, 17) such as sodium fluoride.

Franz and Keplinger (38) describe a continuous nitration process for making trinitrophenylmethylnitramine (tetryl), starting with dinitromethylaniline. The dinitromethylaniline is dissolved in 66° Bé. sulfuric acid, and this solution and the nitrating acid are fed simultaneously into a U-shaped nitrator, which is described.

During World War II the Germans (92) used considerable monomethylamine nitrate, which was prepared by reacting monomethylamine with 66% nitric acid and purified by recrystallization.

Methods for preparing the fourteen mononitronaphthylamines were reviewed by Hodgson and Hathway (52), who discuss these compounds as regards general utility, convenience, and the best one selected where choice is possible. The article includes sixty-three references.

Spaeth (85) describes a process for the production of nitrourea in which urea is dissolved in a crystallizing medium, such as acetic acid, and converted it to urea nitrate by the addition of nitric acid. Without separating the urea nitrate from the reaction mixture, the product is converted to nitrourea by treatment with a dehydrating agent, such as acetic anhydride.

The nitrating and dehydrating agent selected for nitration depends on the compound to be nitrated and the desired degree of nitration. The simplest nitrating agent that may be used is nitric acid. Unfortunately, but few compounds can be nitrated with straight nitric acid because the water liberated during the reaction interferes with the nitration reaction and may even reverse it—that is, the process is not in equilibrium. Pentaerythritol is one of the few compounds that may be completely nitrated with nitric acid alone, provided the strength of the acid does not drop below about 80%.

Generally some means of reducing the activity of the water liberated must be provided. Sulfuric acid is the most common and cheapest dehydrating agent used for fixing the water liberated during the nitration reaction. The strength of the nitrating acid and the amount of sulfuric acid required depend on the compound being nitrated and the desired degree of nitration. The ratio of sulfuric acid to water in the final acid (spent acid) after the nitration is complete is termed the dehydrating value of sulfuric acid (commonly designated as D.V.S.), which may be expressed by the following equation:

$$\text{D.V.S.} = \frac{\% \text{ actual } H_2SO_4 \text{ in mixed acid}}{\% \ H_2O \text{ of reaction} + \% \ H_2O \text{ in mixed acid}}$$

based on 100 pounds of the original mixed acid. Groggins (42) discusses the method of calculating dehydrating value of sulfuric acid and gives examples.

The dehydrating value of an acid for the nitration of a particular compound is generally fixed by experimentation, so that the maximum yield of nitrated product is obtained with the least amount dissolved in the spent acid and at a minimum cost. Generally if the water in the spent acid is held about constant and the temperature is constant, the solubility of the nitrated product in the spent acid increases as the ratio of sulfuric acid to nitric acid increases. In the nitration of glycerol, for example, the sulfuric acid should exist as the monohydrate in the spent acid. Hence, only enough sulfuric acid should be used to maintain the reaction in equilibrium.

In addition to sulfuric acid, other dehydrating agents such as acetic anhydride, phosphorus pentoxide, and boron trifluoride may be employed. Acetic anhydride reacts with water to give acetic acid, and the use of phosphorus pentoxide is analogous. When boron trifluoride is used, a complex is formed with the water (Thomas and colleagues, 91). Another means of taking up the water of reaction is the use of nitrogen pentoxide as a nitration agent. This agent is dissolved in an inert solvent, such as chloroform. Part of the pentoxide reacts with the water liberated to give nitric acid, which is fixed with sodium fluoride as discussed by Caesar and Goldfrank (17).

The cost of nitration depends largely on the procedure used to remove water from the system and regeneration of the dehydrating agent. The lowest costs are attained when straight nitric acid is used, followed by neutralization or by feeding the weak nitric acid to an absorption tower. Generally this is not feasible, and the next cheapest nitrating agent is a mixture of nitric and sulfuric acids, which are subsequently recovered from the spent acid.

Other dehydrating agents—for example, acetic anhydride—are expensive because of the high cost of regeneration. Furthermore, acetic anhydride or other dehydrating agents may introduce undesirable side reactions that render the purification of the end product difficult. Hence, they should be used only where nitration cannot be readily effected by other means, or when the extra cost can be accepted because of the end use of the product. If this process is to be economical, the tonnage of the product made must be such that a large-scale recovery can be operated.

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OXIDATION

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BY FAR the most important and interesting commercial project on the manufacture of chemicals from petroleum hydrocarbons by oxidation during the period under review is that of the Celanese Corporation of America at Bishop, Tex. This $20,000,000 plant, based on the controlled, noncatalytic oxidation of propane-butane hydrocarbons is reported to consume over 50,000,000 gallons annually of these light petroleum gas hydrocarbons together with very large volumes of natural gas used as processing fuel (16, 18). Currently over 300,000,000 pounds of chemicals, including formaldehyde, acetic acid, methanol, and propanol, are being shipped annually and developments are under way to recover other products. Plant costs and production statistics for some petrochemical operations have been reported (61).

Another approach to the commercial use of petroleum oxidation is shown in the announcements of plans for the McCarthy Chemical Company plant at Winnie, Tex. (17). A direct oxidation technique has been developed for use in connection with a plant to manufacture aromatic hydrocarbons and ethylene with a projected volume of 600,000 to 900,000 pounds per day of acetaldehyde and formaldehyde.

The crude liquors from the Cities Service Company's natural gas oxidation plant at Tallant, Okla., have been reported to contain 35% methanol, 20% formaldehyde, 5% acetaldehyde, and varying amounts of higher alcohols and aldehydes plus acids (238). Ion exchange resins are used in the purification of the formaldehyde to resin grade; the objectionable impurities are mainly acids (44).

The use of hydrogen bromide as a gas phase catalyst in the direct oxidation of hydrocarbons has been shown to result in high yields of oxidation products (198). With propane, yields of 76 mole % acetone plus 11.2 mole % propionic acid were obtained and with butane, yields of 52 mole % methyl ethyl ketone and diacetyl. Hydrogen bromide plus a bromide of a straight-chain paraffin permits oxidation of ethane, propane, and cyclopentane to oxygenated compounds of the same number of carbon atoms (186). It has been found advantageous to effect the reactions in glass or silica vessels coated with an oxide of boron. By bringing the reaction mixtures containing hydrogen bromide into contact with an olefin as soon as formed, the by-product bromine reacts with the olefin to give an aliphatic bromide useful in the processes employing hydrogen bromide catalyst (234).

Other vapor phase oxidation catalysts include such "proknocks" as alkyl nitrates, nitrites, or nitro compounds, nitric oxides, nitric acid, and potassium permanganate solutions (8, 168, 178, 228).

The catalytic oxidation of methane or natural gas at high pressures (153, 154) has been re-examined in experiments conducted by the Canadian Bureau of Mines (20). Pressure oxidation of propylene was reported to give glycerol and propylene glycol and of ethylene to give ethylene glycol directly (171).

Apparatus and methods for the determination of the ignition temperatures of combustible liquids and gases have been described which differ from those customarily used and give values differing from those customarily obtained (205).

Considerable attention is being given in the United States to the possibility of high temperature oxidation of natural gas hydrocarbons to produce acetylene. Data on the cost by this method based on an estimate for a proposed plant in Heydebreck, Germany, show that the credit values assigned to the tail gases, consisting of hydrogen and carbon monoxide, are of the utmost importance in determining the acetylene cost on basis of United States practice of the process (26). By reversing the approach, it is possible to think of acetylene as a by-product of the oxidation of natural gas for manufacture of hydrogen–carbon monoxide mixtures for Fischer-Tropsch synthesis of liquid fuels.

The uncatalyzed reaction of steam and natural gas for production of hydrogen–carbon monoxide mixtures has been found by the Bureau of Mines to lead to carbon deposition even at temperatures as high as 1500° C. and with steam ratios as high as 5 to 1 (81).

Direct oxidation of methane (natural gas) with "tonnage" oxygen about 95% pure is assuming tremendous importance in connection with the production of hydrogen–carbon monoxide synthesis gas, raw material for the American modified Fischer-Tropsch synthesis of liquid fuels and chemicals (38, 112, 201). This receives more attention in the section on Tonnage Oxygen.

The importance of organic peroxides, particularly for use as polymerization catalysts, has stimulated research in methods of production. Under conditions of partial oxidation of certain hydrocarbons by air or oxygen in the liquid phase, peroxide content may reach values from 0.5 to 5.0%, but by suitably adjusting conditions concentrations up to 20% and more in the hydrocarbon may be obtained. Means have been developed for the commercial production and recovery of such peroxides, sold by the Union Oil Company as Uniperox products (70, 100).

Hydrogen bromide has been found to catalyze the oxygen oxidation of tertiary carbon atoms to hydroperoxides. Thus, the reaction of a mixture of substantially equimolar proportions of isobutane and oxygen at 150° to 200° C. and superatmospheric pressure in the presence of hydrogen bromide results in formation of *tert*-butylhydroperoxide and di(*tert*-butyl) peroxide. Isopropyl benzene similarly reacts to form a *tert*-hydroperoxide (199, 235). It has been found advantageous to have the vessels composed of glass coated with oxides of boron.