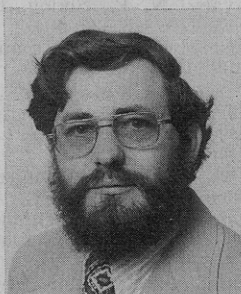


Ambient Curing Polymer Coatings

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The coatings industry has been slow to adopt new ambient curing systems. Air-oxidizable coatings, based on unsaturated oxidizable fatty acids, have served the coatings industry well. These products continue to dominate a large percentage of the air-drying coatings market today. However, the adhesives and sealants industries have introduced several novel curing mechanisms which could signal forthcoming changes in the technology of air-drying coatings.

It is difficult to find reviews under the specific heading of ambient film-forming reactions. Various segments are usually discussed in conjunction with other systems under the general heading of a particular class of compounds. For example, siloxane formation under ambient conditions is usually described in articles that also discuss silicone compositions which require elevated curing temperatures under the heading of silicone resins. It is the objective of this review to introduce the coatings chemist to recent advances in the chemistry of ambient curing systems. We intend to give a summary accounting of the recent literature on the subject and to emphasize technology which might lead to future improved air-drying coatings.

All of the curing mechanisms discussed in this review involve chemical film-forming reactions. However, the technology of ambient curing polyurethanes is omitted since several excellent review articles dealing with this subject are available (7, 12). We do not desire to minimize the importance of air-curing polyurethane systems. Lacquers and air-drying latices are also excluded since, by definition, these types of coatings do not undergo chemical conversion after they have been deposited as films.

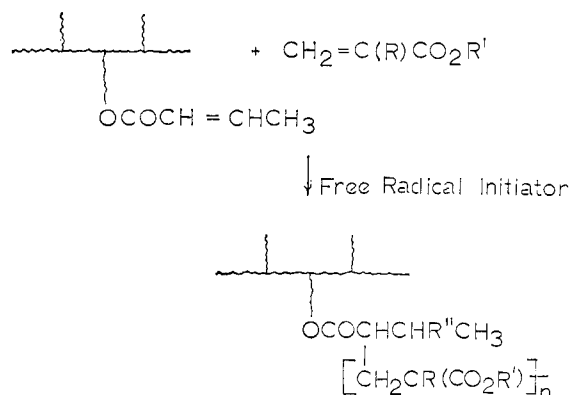
Air Oxidation

With the application of modern science the actual chemistry of the autoxidation mechanism has been elucidated (35). More recently researchers have attempted to modify non-oxidizable resins, such as acrylic polymers, with unsaturated fatty acids as a means of introducing ambient cross-linking potential into these polymers. The modified resins are stable single packages in the absence of oxygen. This is an important advantage of this type of polymer since most other ambient curing systems require two coreactable components, each in its separate container. In typical two-package formulations

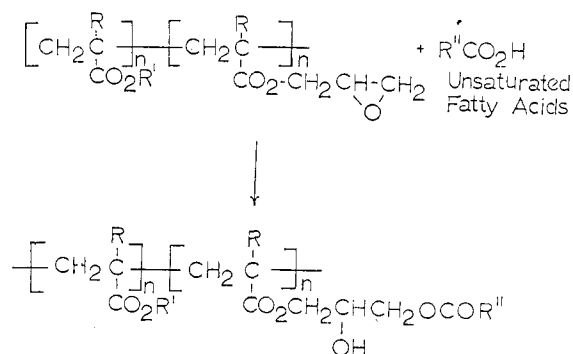
The cross-linking mechanisms reviewed include air oxidation, siloxane formation, metal chelate cures, and nitrile oxide curable systems. The recent literature pertaining to these mechanisms and their possible utility in coatings, sealants, and adhesives is reviewed.

a catalyst or another component is required to initiate the ambient cross-linking reaction.

Alkyd-acrylic copolymers are prepared by a number of synthetic procedures. A technique has been developed in which styrene and acrylic monomers can be copolymerized with an oxidizable alkyd containing crotonic acid unsaturation. The resultant copolymer contains an alkyd backbone with pendent acrylic chains (34).

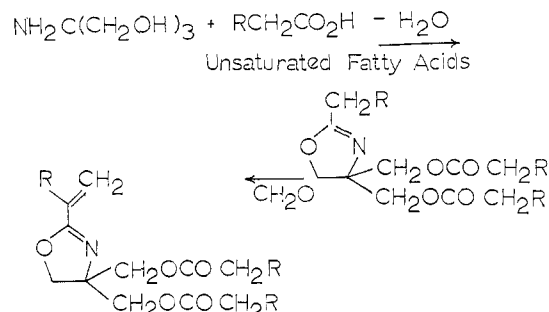


Alternatively, several recent patents describe methods for preparing acrylic polymers containing pendent fatty acid chains which undergo air oxidation to yield cross-linked films. An acrylic polymer containing glycidyl functionality or a homopolymer of, for example, glycidyl methacrylate is used. The reaction of the epoxide groups in these polymers with unsaturated fatty acids imparts air-drying (cross-linking) properties to these resins (9-11).



The hydroxyl groups in the product can be treated with isocyanates or a variety of acylating agents (9-11). The acylated modification is reported to enhance the pigment-wetting properties and improve the gloss of coatings formulations (15).

The reaction product of unsaturated fatty acids, tris(hydroxymethyl)aminomethane, and formaldehyde yield products called vinyloxazolines (31). Vinyloxazolines containing unsaturated fatty acids are copolymerized with acrylic monomers to yield light-colored resins which are cured by air oxidation to tough films (27). Enamels based on oxazoline drying oils-acrylic copolymers are reported to give an excellent balance of properties for air-drying coatings applications.

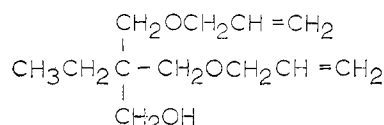


Coatings of this type are said to be especially useful as automotive refinish enamels.

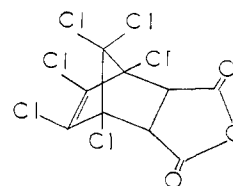
The above examples illustrate a possible trend in the technology of air-oxidizable coatings. There seems to be a de-emphasis of the alkyd portion of these vehicles. Thus, the technology has evolved from alkyd resins to alkyd copolymers to fatty acid modified polymers. In some applications, the last type of vehicles may contribute a better overall balance of properties to coatings than are provided by straight air-oxidizable alkyds.

From a durability standpoint the weak link in autoxidative cured systems is the unsaturated fatty acids. The next step in the evolution of these coatings might involve replacing the unsaturated fatty acids with another moiety which will cross-link on exposure to air.

In U. S. Patent 3,491,065 the authors claimed that polymers containing allyl ethers, for example, trimethylolpropane diallyl ether, undergo air oxidation to give films exhibiting excellent color retention properties (24).



These polymers probably oxidize in the presence of driers in a manner analogous to that of those containing unsaturated fatty acids. The trimethylolpropane diallyl ether is introduced into polyesters *via* the condensation of the free hydroxyl group on the monomer with an acid group in the polyester. However, it appears necessary that the polyester contain hexachloro-*endo*-methylenetetrahydrophthalic acid or its anhydride for good air-oxidizable properties. It is not immediately obvious why this should be true (24).



Allyl glycidyl ethers are polymerized with other oxirane compounds to form polyethers which when blended with polyesters and driers yield films which cure *via* the autoxidation mechanism. The polyester is not required to contain oxidizable unsaturation; the allyl ether group provides sufficient cure potential to give good films (39).

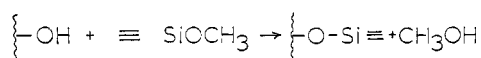
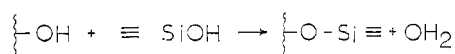
The preceding examples suggest that allyl ethers can be incorporated into polymers which will air-dry. Although the references cited are limited to polyesters, allyl groups might also be introduced into other types of polymers in the future to provide unique coatings.

Thus we have arrived at oxidizable polymeric compositions which do not depend on the oxidation of unsaturated fatty acids. This may prove to be a significant step forward in the art of air-oxidizable coatings systems.

Ambient Curing Silanes

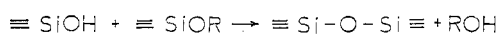
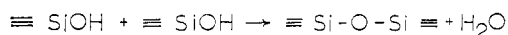
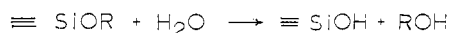
The first silicone resins designed as protective coating vehicles were developed in the middle 1940's and their excellent ultraviolet and oxidation resistance properties were soon recognized. The early silicone organic coatings were simply based on cold blends of a silicone resin and, for example, an alkyd. These coatings exhibited excellent color and gloss retention.

While cold blending is the simplest method of preparing silicone-modified resins, copolymerization of silicone intermediates with hydroxyl functional organic resins eliminates the often encountered compatibility problem. Thus, it has been shown that silicone-organic copolymers can be formed by the reaction of the excess hydroxyl groups in an alkyd with silanol ($\equiv\text{SiOH}$) or methoxy functional silicone intermediates (2, 8, 17, 20, 21, 23).



Again, copolymers of this type show superior weathering properties when compared with straight alkyd compositions. These properties have made silicone-modified alkyds (both cold blends and copolymers) particularly important in the area of air-drying maintenance paints. However, the above coatings depend on an air oxidation mechanism (or some other ambient cross-linking reaction) for cross-linking rather than an ambient siloxane formation curing mechanism. In other words, the silicone portion of the coating is unreactive in the cross-linking stage of film formation.

Resins modified with reactive silanes are of more recent interest. Materials of this type can be made to undergo siloxane formation in the presence of a catalyst and moisture at room temperature. Reactive silanes, such as alkoxy-silanes, form silanols in the presence of moisture and a suitable catalyst, such as dibutyltin dilaurate, which undergo a condensation reaction with either another silanol or an alkoxy-silane to form siloxane (silicone) linkages. The chemistry of silicones and organosilicon compounds has been reviewed by Faulkner (16) and others (13, 28).



The coatings industry has been slow to adopt reactive silane-modified polymers which cure in the ambient atmosphere. This reluctance might be based on the high cost of

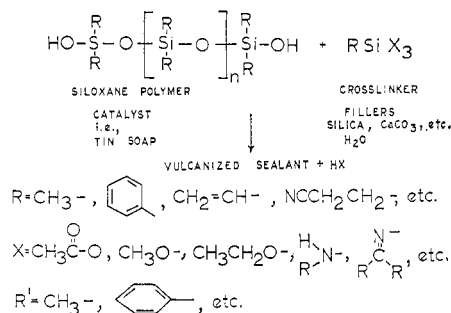


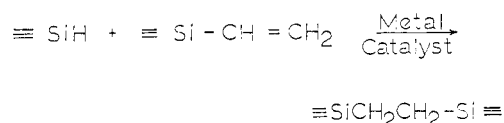
Figure 1. Room-temperature vulcanizable sealants

reactive silane intermediates and also the fact that coatings of this type may have to be marketed as two-component products. However, the silane-curing mechanism may hold considerable potential for the coatings industry. On the other hand, adhesives and sealants which are cured through reactive silane functionality at room temperature are being marketed (18, 37). Since the chemistry involved in these products might also be applicable to coatings, a discussion of these products is given.

Room-temperature vulcanizable (RTV) silicone sealants are grouped into two major classifications in terms of the chemistry involved in the cure. The first, and most important, of these involves the condensation of a reactive silanol group on a silicone polymer with polyfunctional reactive silanes, which is summarized in Figure 1. These materials can be marketed as single-package compositions if water is rigorously excluded from the mixture. The polymeric silanols are sufficiently unreactive with the cross-linking agents such that cross-linking does not occur until the cross-linker is hydrolyzed in the presence of water to a silanol which reacts with the polymeric silanol to give a new siloxane linkage.

Compositions of the above type are also marketed as two-package products. Generally, one part consists of a mixture of polymer, filler, and cross-linker and the second component is a metal soap catalyst. Water does not have to be rigorously excluded in the manufacture of these products since the catalyst is separated from the other ingredients.

The second major class of RTV silicones involves the metal-catalyzed addition of polyfunctional polymeric silicone hydrides to vinyl-containing polysiloxanes



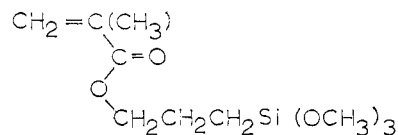
The catalysts required for conversions of this type are usually expensive, *e.g.*, platinum salts. Thus economic limitations are imposed on these systems.

An extensive review of the abundant patent literature on the subject of room-temperature curing organopolysiloxanes is beyond the scope of this review. Much of the patent literature deals with small structural changes in the siloxane polymer and the cross-linking agent. However, there are some patents which illustrate novel chemistry or technology that might be useful to the coatings chemist.

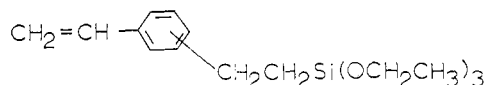
The cross-linking agents given in Figure 1 all contain groups which are relatively easily hydrolyzed to reactive silanols. In addition to these groups, several other functional units have appeared in the patent literature which are suggested to be useful cross-linkers. These include the imidatosilanes (14), aminoxy-silanes (29), and phosphatosilanes (29) (Figure 2).

In general, all of these compounds are prepared from an organic moiety containing an active hydrogen and the proper silicon precursor, *e.g.*, a halosilane.

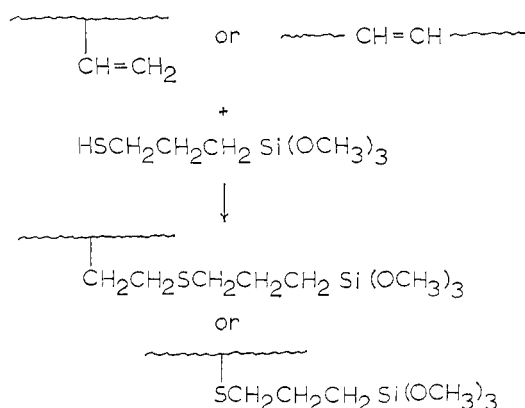
Polymers containing carbon backbones and pendent silicone functionality might be especially interesting to the coatings chemist. A British patent (22) describes acrylic polymers modified with, *e.g.*, 3-(trimethoxysilyl)propyl methacrylate



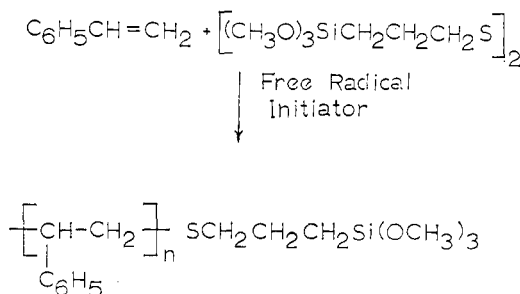
Polymers of this type are cured with a tin catalyst at room temperature to give cross-linked products useful as pressure-sensitive adhesives. Vinyl polymers containing 2-(vinyl-phenyl)ethyltriethoxysilane have also been described which cure in the ambient atmosphere to give rubberlike gels (1).



Several interesting patents (30, 33, 36) describe procedures for modifying butyl rubbers, acrylics, and alkyds with reactive silane functionality. All of these procedures utilize silanes functionalized with sulfur, *e.g.*, mercaptopropyltrimethoxysilane, $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, or its disulfide, $[(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{S}]_2$. The mercaptan is grafted onto unsaturation in the polymer by standard free-radical methods to give functionalized polymers capable of cross-linking in the ambient atmosphere.



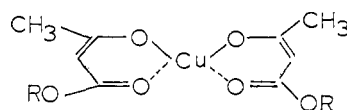
Alternatively, both the mercaptan and the disulfide can be used as chain-transfer agents in the polymerization of styrene or acrylic monomers to give polymers terminated with alkoxy-silanes (30, 33)



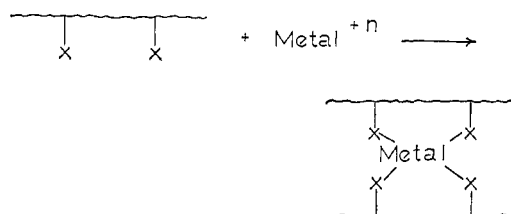
Polymers of this general type are useful as ambient curing coatings and sealants.

Metal Chelates

The term chelate, by definition, refers to a cyclic metal complex of which the copper chelate of acetoacetate is a classic example

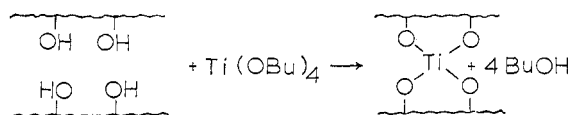


Chelating polymers are then polymers capable of forming cyclic metal complexes through some suitable basic site on the polymer to give what may be a cross-linked system as illustrated by



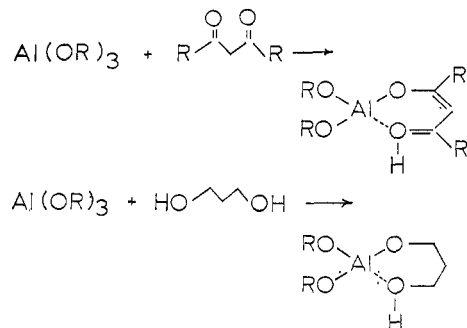
The various aspects of chelating polymers are contained in a recent review with an excellent list of recent references (40). Curing mechanisms occurring through the ligand-metal ion bond could replace some of the conventional cross-linking mechanisms and give improved film properties. It is also significant to mention that in most cases the functionalized polymer and the chelating metal are stabilized in the presence of each other to give single-package products.

Pressure-sensitive adhesives, based on this curing mechanism, are cross-linked at room temperature to give adhesives with improved plasticity, etc. In these applications metal alkoxides such as tetrabutyl titanate are used to cross-link acrylic resins containing, for example, pendent hydroxyl groups (3)



The preceding compositions are relatively stable as single packages in the presence of alcohol but rapidly cross-link in the absence of alcohols. The compositions are unstable in the presence of water, which might suggest that adhesive films have poor hydrolytic stability.

Carboxylic acid containing polymers are cross-linked with aluminum alkoxide compounds to provide useful coatings (19). The aluminum alkoxide compounds of this invention are formed by the reaction of an aluminum alkoxide and 1,3-diols or enolizable 1,3-dicarbonyl compounds



In the curing reaction, the carboxyl groups of the polymer complex with the aluminum alkoxide as the diol or the 1,3-dicarbonyl compound evaporates. Again, these materials are

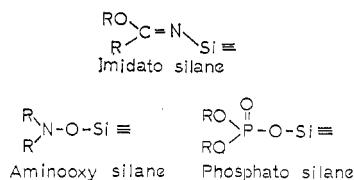
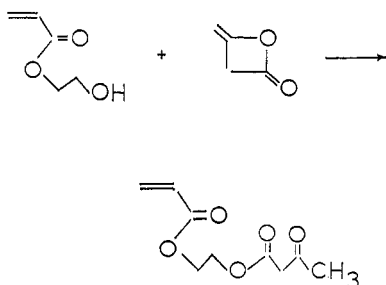


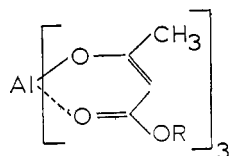
Figure 2. Miscellaneous reactive silanes

stable as a single package in the presence of aliphatic alcohols. Films of the aluminum chelated resins provide good hydrolytic stability and in general are comparable to thermosetting acrylic films.

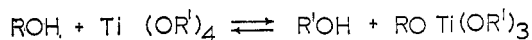
In another variation, chelated films are obtained from the interaction of polymers containing acetylacetate groups and the acetoacetates of polyvalent metals (25, 26). Monomers containing the acetylacetate group may be derived from the reaction of, for example, hydroxyethyl acrylate and diketene



Alternatively, hydroxyl functionality in a resin is allowed to react with diketene to give the desired functionality (38). According to U. S. Patent 3,607,834, polymers modified with acetylacetate groups are cured with aluminum triacetylacetonate to give insoluble cross-linked films suitable for many coatings applications (25)



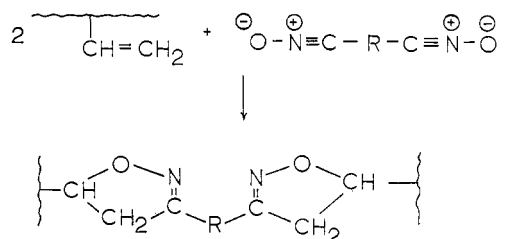
Since the chemical principles involved in the metal chelate cures might have broad utility in ambient curing systems, a brief discussion of these principles is in order. In the presence of alcohols or other stabilizing agents, the reactive metal cross-linker undergoes ligand exchange with the stabilizer as illustrated by



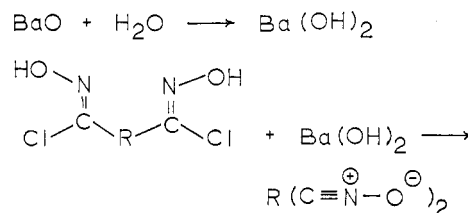
The potential chelating sites on the polymer are left unbound because of unfavorable energetic and concentration (chelating sites are less abundant than reactive stabilizing groups) factors. Thus, a kinetic, rather than a thermodynamic product distribution exists in the presence of stabilizer. However, as the concentration of stabilizer is reduced by evaporation during film formation, the thermodynamic product becomes favored (formation of polymeric metal chelate). The stability of the cured film depends on the irreversibility of this reaction, which, at least in part, is dependent on the magnitude of the thermodynamic stabilization. In summary, the success or failure of systems of this type depends on a delicate balance of kinetic and thermodynamic properties—kinetic stabilization in the paint can *vs.* thermodynamic stabilization in the paint film.

Miscellaneous Material

A unique cross-linking chemistry has recently been developed by Breslow and Brack (4-6, 32). This chemistry, in our opinion, represents an ingenious advance in the art of ambient curing systems. The curing composition involves a polymer containing pendent unsaturation which is cross-linked with a bis(nitrile oxide). In the cure reaction, the nitrile oxide adds across an olefinic bond in a 1,3-dipolar addition to form 2-isoxazoline cross-links. Single-package stability is achieved by using a nitrile oxide precursor. The nitrile oxide



precursor is activated by bases such as barium hydroxide which is formed by the reaction of atmospheric moisture and barium oxide



Thus the composition is stable as a single package and activated after application by atmospheric moisture. The nitrile oxide precursors are prepared according to rather elaborate patented procedures (6). Polymeric olefins cured by nitrile oxides are said to be useful as sealants and caulking compounds.

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CATALYST SECTION

Ammonia Formation in the Nitric Oxide—Methane Reaction

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The catalytic reduction of nitric oxide using methane was studied in a static system over a silica-supported platinum catalyst. At 350°, ammonia was the primary product while at 250° nitrogen was predominant. It was found that an increase in nitric oxide concentration increased the rate of nitrogen formation at 250° while at 350° the ammonia formation was increased. The complete absence of nitrous oxide from the reaction products tends to exclude HNO as a precursor to ammonia formation. It was concluded that a catalyst dissociative chemisorption of hydrocarbons promotes ammonia formation.

Variables affecting the formation of ammonia in the catalytic removal of nitric oxide from automobile exhausts have recently become the subject of intense investigations. In a dual-bed catalytic muffler, nitrogen oxides are reduced over the first bed. Air is then added to the effluents and the unburned hydrocarbons and carbon monoxide are oxidized over the second bed. This approach appears to be chemically sound; however, analytical determinations of nitric oxide concentrations of exhaust effluents show relatively large concentrations of nitric oxide, whereas concentrations of nitric oxide in the effluents from the first bed are relatively low. The problem centers around the reoxidation of ammonia in the second stage. Within the usual temperature range of automobile exhausts, ammonia and nitrogen are the main products in the catalytic reduction of nitric oxide with hydrogen, and since the presence of ammonia is undesirable, the study of the variables which affect the formation of ammonia has become a pressing problem. Both hydrogen and unburned hydrocarbons are present in fairly large concentrations in

automobile exhausts so that reduction over the first bed can be carried out with little difficulty. Products formed in the catalytic reduction of nitric oxide with hydrogen have been the subject of many investigations, however relatively few studies have appeared in the literature in which hydrocarbons are used as a reducing agent. It is to this aspect of the problem that we addressed ourselves in this investigation.

The variables which affect ammonia formation when hydrogen is used as a reducing agent have been carefully studied (Ayen and Peters, 1962; Jones, *et al.*, 1971; Shelef and Gandhi, 1972). The production of ammonia depends critically on both temperature and nitric oxide concentration. At temperatures below 200°, besides nitrogen, the major nitrogen-bearing product is nitrous oxide with only traces of ammonia being formed. The concentration of ammonia increases rapidly with temperature usually going through a maximum between 400 and 500°, depending on the catalyst used, due to the decomposition of ammonia to molecular nitrogen and hydrogen. Ammonia conversion also increases with decreasing