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MANGANESE-MODIFIED ASPHALTS: CHEMISTRY OF THE CURING REACTION, ITS EFFECT ON PROPERTIES, AND EVIDENCE FOR MANGANESE INACTIVATION FOLLOWING CURE

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16. Abstract

ABSTRACT

The chemical reactions and reaction kinetics of asphalt modified with a patented modifier supplied by Chemkrete Technologies, Inc. were investigated. The modifier, a manganese-carboxylic acid complex, has been shown to cause a rapid reaction with atmospheric oxygen when the modified asphalt is exposed as thin films. This reaction produces paving mixtures with increased stiffness and tensile strength. In the present study, a good correspondence was found between the manganese-induced oxidation reaction (cure) and the increase in asphalt viscosity. The rapid, modifier-induced reaction with oxygen and the corresponding rapid increase in viscosity ceased following cure. The incremental increase in viscosity on cure was found to be governed by the asphalt oxidation chemistry, with the manganese modifier apparently being inactivated at the end of the cure by diketones formed during the manganese-catalyzed oxidation reaction. The chemistry of the manganese inactivation on cure was investigated in detail. Results of the study provide further confirmation for the mechanism of formation of anhydrides in asphalt.

17. Key Words Modified asphalt, manganese modification, Chemkrete, curing reaction, asphalt oxidation, anhydride formation, oxidation mechanisms

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INTRODUCTION

A patented modified paving composition (1) has been introduced to the paving industry. The modified composition, called Chemkrete, contains an asphalt that has been pretreated with an asphalt-soluble metal complex of manganese. In the absence of oxygen (air), as in bulk storage, the modifier is inactive. When a thin film of asphalt is exposed to air, as in a permeable asphalt paving mixture, the modified asphalt undergoes a rapid metal-induced reaction with atmospheric oxygen that markedly increases binder consistency. This reaction produces a "cured" paving composition with significantly increased stability and tensile strength characteristics (2). Properties of the modified paving mixtures are reported elsewhere (2 - 4). This report focuses on the chemistry of the Chemkrete modification.

Prior work at the authors' laboratory (5) in a cooperative asphalt research program funded jointly by the Department of Energy (DOE) and the Federal Highway Administration (FHWA) showed no significant differences in the major oxygen-containing chemical functional groups formed in unmodified asphalts as a result of air-oxidative aging and those formed in the corresponding cured, manganese complex-modified asphalt. It appeared that the behavior of modified and unmodified asphalt toward reaction with atmospheric oxygen was more a matter of reaction rate than of differences in the type of oxidation reactions. Of significance, however, was the observation that the metal-induced reaction with atmospheric oxygen ceased abruptly after a certain level of reaction had occurred. Further, the termination of the metal-induced reaction was found to be independent of the final viscosity of the asphalt, i.e., softer asphalts produced correspondingly softer cured products, and the termination of the reaction appeared to be related to the level of oxidation achieved in the modified asphalt. These results suggested that the manganese complex was inactivated at the end of the cure by chemical or physicochemical means. Following cure, the subsequent reaction of the modified asphalt with atmospheric oxygen was found to be similar to that of unmodified asphalt.

Obtaining further evidence to support the inactivation of the manganese following cure was considered an important objective because excessive hardening of the asphalt following cure would likely produce pavement mixtures with undesirable long-term durability. To answer the questions regarding manganese inactivation and to obtain further information on the kinetics of the curing reaction and its chemistry, the present studies were initiated. Most of the findings reported were obtained under a DOE-FHWA cooperative research program with these findings further substantiated and quantified in a followup study (6) sponsored by Chemkrete Technologies, Inc. For completeness of reporting, the results of the two studies are combined in this report.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Asphalts

The earlier phases of the work were conducted using two paving-grade asphalts, an AC-5 (B-3037) and an AC-20 (B-3035), obtained from the same source so that their chemistry would be similar. These widely studied asphalts were from the Bureau of Public Roads viscosity graded series (7). In later parts of the study, Cosden AC-5 and AC-20 asphalts from American Petrofina, and Wood River AC-5 and AC-20 asphalts from Shell Oil were utilized (4). The specific asphalts used for various phases of the study are identified in the text.

Manganese Modifier

The earlier phases of the study utilized an oil-based manganese complex identified as type 150.40 by Chem-Crete Corporation of Menlo Park, California. This modifier formulation predates, although it is reportedly similar to, the product later marketed by the Lubrizol subsidiary, Chemkrete Technologies, Inc. Type 150.40 modifier reportedly contained a nominal 2% manganese. When the authors analyzed it using functional group analysis techniques (8) it was found to contain about 2.3% active manganese based on an assumed complex between valence 2 manganese and carboxylic acid. The modifier was typically added to the asphalt in a ratio of 1 part of modifier to 15 parts of asphalt to yield a modified asphalt containing 0.125% manganese (6.25% of the oil-based modifier).

In some experiments, an even earlier Chem-Crete Corporation modifier concentrate, identified as Type 125.3, was used. This concentrate consisted of an oil-based modifier preblended with asphalt to yield the concentrate that was added to asphalt in the ratio of 1 part concentrate to 9 parts asphalt. The sample of this concentrate used by us, and reported to contain a nominal 2% manganese, showed 1.8% active manganese as analyzed by the functional group technique previously mentioned. Typically, an asphalt modified as just described would contain a nominal 0.2% manganese.

In later experiments, an asphalt modifier identified as CTI-101™ and supplied by Chemcrete Technologies from production sources, was used. This oil-based manganese modifier contained 2% manganese. Thus, an asphalt modified with 6.25% of this modifier contains 0.125% manganese.

Aging, Curing, and Asphalt Recovery Procedures

Typically asphalts were aged as a uniform thin layer coated 5% by weight on 20-40 mesh Ottawa sand to allow ready access of air to the asphalt. The asphalt-coated sand was fabricated into cylindrical briquets 43 mm in diameter and 19 mm thick using a mold and press as previously described (5). Two methods of preparing the asphalt-coated sand were used, a hot-mixing method and a cold-solvent method.

In the hot-mixing method, which to some degree simulates the aging that occurs in a hot-mix plant, the necessary weighed amounts of asphalt and aggregate were preheated to 150°C in an oven. The hot aggregate was added to the asphalt and the mixture throughly blended. Briquets were then prepared.

The cold-solvent aggregate coating technique was used when it was desired to avoid oxidation or "cure" of the asphalt during briquet preparation. In the cold-solvent coating technique, the asphalt was dissolved in the minimum amount of benzene needed to provide good coating of the Ottawa sand (approximately 1:1, volume percent benzene: weight percent asphalt). After addition of the Ottawa sand, the benzene was evaporated in a hood while the mixture was stirred for a short time in an evaporating dish at room temperature. Briquets were immediately made using a cold mold and placed in a freezer until the next day when curing experiments were started.

In kinetic aging studies, sufficient replicate briquets were prepared so that individual briquets could be removed from the oven for analysis as a function of time.

Following aging, asphalts were extracted from the briquets immediately after their removal from the oven; otherwise, briquets were placed in the freezer until extraction. Asphalt was extracted from the Ottawa sand by soaking the briquet in a mixture of 95% benzene and 5% ethanol for 30 minutes, filtering the mixture, and washing the aggregate with a benzene-ethanol mixture until the filtrate was colorless. The solvent was removed using a vacuum rotary evaporator at 120°C. Solvent content of the recovered asphalt was monitored to ensure that less than 0.2% was present by following the intense benzene infrared band at 670 cm^{-1}. Following recovery, the extracted asphalt was maintained in a freezer to minimize further oxidation until chemical and physical properties were measured.

Analytical Techniques

Functional group analyses were made using differential infrared spectroscopic techniques combined with selective chemical reactions as previously described (8, 10). Viscosities at 60°C were measured using a Rheometrics mechanical spectrometer (5) equipped with 25-mm plates spaced 1 mm apart. Shear frequencies of either 0.01 or 0.1 radians/second, as required to obtain near Newtonian flow, were used during the measurements. Additional specialized techniques used in the study are described in the text as appropriate.

FUNDAMENTALS OF ASPHALT OXIDATION

The manganese-induced reaction of asphalt with atmospheric oxygen has been shown to be similar to normal air oxidation in paving asphalts (5), except that the reaction rate is many times faster. Also, as will be proposed in this report, the manganese is apparently inactivated at the end of the cure by a specific chemical functionality produced in the asphalt during the cure. Therefore, the following review of the chemistry of asphalt oxidation is presented to provide the necessary background for the discussion of the chemistry of the manganese-induced reaction in asphalt.

Except for the oxidation of organic sulfides in asphalts to sulfoxides, the major oxidation reaction in asphalts at temperatures below 150°C is the oxidation of hydrocarbon components of asphalt molecules. A simplified, generalized scheme proposed (11) for the oxidation of these hydrocarbon components is shown in Figure 1. Based on this reaction scheme, ketones are the major functional group formed, which is consistent with generally accepted hydrocarbon oxidation mechanisms. In the reaction scheme the symbol R may represent either a hydrogen atom or an alkyl group. The reaction is initiated by the abstraction of a hydrogen attached to a benzylic carbon of an asphalt molecule (I) to form a free radical (II). The free radical reacts with atmospheric oxygen to form a peroxy radical (III). This in turn may rapidly decompose to form a ketone (IV), or, more likely, abstract a hydrogen atom from the benzylic carbon of another asphalt molecule (V) to form a hydroperoxide (VII). The asphalt free radical formed (VI) can react with atmospheric oxygen to repeat the process. The hydroperoxide is rather unstable and may decompose to form either a ketone (VIII) or an alkoxy radical (IX). The alkoxy radical may rapidly decompose to form a ketone (X). This mechanism is admittedly oversimplified and minor amounts of other oxidation products not shown are undoubtedly formed. However, it adequately accounts for the major hydrocarbon oxidation product, ketones. Ketones have been positively verified (12) as the major oxidation products in oxidized asphalt. Smaller amounts of anhydrides are also formed (13) in the later stages of oxidation. Under certain conditions alkyl groups may oxidize to the carboxylic acids, however, only small amounts of carboxylic acids and no measurable esters (13) have been found in laboratory or pavement-aged asphalts. It appears that the hydrocarbon oxidation reaction predominantly stops at the ketone.

The relationship between anhydrides and ketones formed in an asphalt at different levels of oxidation is shown in Figure 2. Significant amounts of anhydrides are not formed until a ketone content of about 0.2 mol L^{-1} has been reached, at which point the rate of anhydride formation begins to increase significantly. Beyond about 0.6 mol L^{-1} for this particular asphalt, the relative rates of ketone and anhydride formation stabilize to form a straight-line relationship with about six ketone functional groups being formed for every anhydride functional group formed. Thus there seems to be an induction period during the early stages of asphalt oxidation before significant anhydride formation occurs. It is important to note with regard to the mechanism of anhydride formation that carboxylic acids, as noted earlier, are not formed in significant amounts. Thus, it would appear that if anhydrides are formed from the oxidation of side chains on aromatic ring systems, then they probably do not form via a carboxylic acid intermediate. It is thus logical to assume that neither physical proximity nor chemical reaction conditions favor the formation of anhydrides in asphalt via oxidation of side chains to carboxylic acids.

A proposed mechanism for the formation of anhydrides, which accounts for the facts just presented, is shown in Figure 3. This mechanism has been proposed by the authors for a number of years, but without definitive evidence. The present study of the chemistry of manganese-modified asphalt produced additional evidence for the reaction scheme in Figure 3, as will be seen as the details of the study are discussed. Only that portion of the asphalt molecule important to the oxidation reaction under discussion is shown in Figure 3. It has been shown (13) that the anhydrides formed in asphalt are of the 1, 8-naphthalic anhydride type, i.e. the anhydride functionality is attached to the 1 and 8 positions of a naphthalene ring moiety of an asphalt molecule. The naphthalene ring system is planer and rigid, and thus imparts specific spacial restrictions or stereospecificity to the functionality attached to the 1, 8-bridgehead position. As the asphalt oxidizes via the random, free-radical process described in Figure 1, ketones are formed at random via the unstable hydroperoxide intermediate by oxidation of side chains attached to aromatic rings of the asphalt molecules. After a period of time a significant concentration of the proposed intermediate shown in Figure 3, with the ketone and hydroperoxide in the 1 and 8 positions, begins to form. Because it takes time during the random oxidation of hydrocarbon side chains to build up a significant concentration of the specific intermediate required, considerable amounts of nonstereospecific ketones form in the earlier stages of oxidation, which account for the induction period shown in Figure 2. According to the mechanism, however, when the specific keto-hydroperoxide forms, it can, by a random process, decompose to form either the 1,8-naphthalic anhydride shown in the lower right of Figure 3 or the 1,8-diketone shown above it. The proposed 1,8-diketone is not distinguishable by the analytical methods used from other ketones formed; however, if it is formed, its concentration is proportional to the concentration of anhydrides formed, the latter being readily quantified by the functional group analysis. The proposed stereospecific diketone is important because it is proposed as a principal factor responsible for the cessation of the manganese-modified reaction in asphalt at the end of the curing period.

KINETICS OF THE MANGANESE-INDUCED CURE

Evaluation of Modifiers Supplied by Chem-Crete Corporation

Previous studies (5) of the chemical and physical property changes as a function of cure time of manganese-modified asphalts in Ottawa sand briquets showed that rapid rate of reaction with atmospheric oxygen, and the corresponding rapid increase in viscosity, ceased after a few days of cure at 45°C. Parallel experiments on an AC-5 (B-3037) and an AC-20 (B-3035) asphalt from the same source showed nearly the same level of oxidation and net increase in viscosity for both asphalts. However, these experiments were conducted using a later-discontinued modifier formulation (Type 125.3 containing 2% manganese and some added asphalt) that yielded a modified asphalt with a relatively high (0.2%) manganese content. Because this high manganese content may produce more stiffening of the asphalt than desired, curing rate data were obtained using the same two asphalts, but using a modifier formulation introduced later (Type 150.40, supplied by Chem-Crete Corporation of Menlo Park, California). This modifier was added 1:15 to asphalt to produce a modified asphalt containing a nominal 0.125% manganese (0.14% active, by analysis). Data in Table 1 show the chemical functional groups formed as a function of cure time at 45°C for both modified and unmodified AC-5s and AC-20s aged in briquets containing 5% asphalt on Ottawa sand. Corresponding selected viscosity data, together with selected viscosity data on the asphalts containing the older, discontinued modifier, are shown in Table 2. Functional group analysis data for the AC-5 asphalt are shown plotted in Figure 4. Chemical data for the AC-20 asphalt were similar to data for the AC-5.

Examination of the data displayed in Figure 4 for the modified and unmodified AC-5 shows that ketones, the major oxidation product, are formed at a rapid rate in the manganese-modified asphalt during the initial stages of the cure. Because the asphalt and Ottawa sand were at 150°C when mixed, some reaction occurred before curing of the briquets was initiated; however, the rapid rate of ketone formation in the modified asphalt compared with that in the unmodified control is evident. The abrupt cessation of the manganese-induced reaction after about four days is also evident. All functionalities shown in Figure 4, except for carboxylic acids, are virtually absent in the asphalts before reaction with atmospheric oxygen. The carboxylic acids originate from the modifier formulation which is a carboxylic acid-manganese complex. Excess acids are present in addition to the amount required to form the complex, in this case about 0.013 mol. L^{-1}. During the cure, free acids are liberated from the complex as seen in Figure 4. This liberation has been identified with the manganese inactivation mechanism that will be discussed later in detail. Significant amounts of anhydrides are also formed in the modified system during cure. Under the mild cure conditions and cure times used, no detectible acids or anhydrides were formed in the unmodified asphalt.

Finally, sulfoxide formation deserves discussion. Compared with other functional groups sulfoxides are easily formed in the unmodified asphalt on oxidation. Sulfoxides in the manganese-modified system reach their highest concentration immediately following cure and then slowly decrease in concentration. These results suggest that during the rapid manganese-induced hydrocarbon oxidation (Figure 1), relatively high concentrations of hydroperoxides are present that are scavenged by the natural sulfides in asphalt to form relatively high concentrations of sulfoxides. Following cure, when the rate of ketone (and thus hydroperoxide) formation is greatly reduced, the sulfoxide concentration decreases because of the thermal sensitivity of the sulfoxides. This interpretation is consistent with reported studies of sulfoxide formation in petroleum residuals (<u>14</u>).

Viscosity data on the AC-5 and AC-20 asphalts after complete cure (50 days) and after an extended aging are shown in the lower section of Table 2. Corresponding ketone contents are shown in parentheses. Before the viscosities were measured the samples were heated until semifluid to destroy molecular structuring (steric hardening) in an attempt to eliminate this complicating factor from the measurements. As expected the viscosities of cured, modified systems are considerably higher than those of unmodified systems. Also, the lower viscosity AC-5 arrived at a correspondingly lower viscosity than the AC-20 upon cure. This fact is extremely important with regard to the stability and low-temperature properties of the modified pavement. Viscosity changes between the 50- and 210-day cure times are believed representative of normal aging of the cured asphalt at 45°C (113°F). Comparison of the 50-day and 210-day data shows considerable increases in viscosity with time, more than seen in the corresponding data for the unmodified asphalts. These results suggest that the long-term aging characteristics of the modified asphalts need further investigation.

Viscosity data from the earlier study using the Type 125.3 modifier, which prompted the study under discussion, are shown in the top portion of Table 2. A comparison of the 50-day aging data for asphalts modified with both the old modifier (used in a ratio of 1:9 with asphalt) and the newer modifier (used 1:15) shows the cured asphalts containing the old modifier have slightly higher viscosities. The viscosity difference, however, is about what would be expected based on the slightly higher manganese content (additional data in this regard will be presented later). Thus, there are apparently no significant differences in the characteristics of the asphalts cured using the two different modifier systems other than those that can be attributed to intrinsic differences in the modifiers.

Evaluation of Modifier Supplied by Chemkrete Technologies, Inc.

In a more recent coordinated study (4, 6) the kinetics and chemistry of the manganese-modified asphalt together with engineering properties on asphalts and laboratory paving mixtures were reevaluated using the current modifier, CTI-101™, in four asphalts, a Texas Cosden AC-5 and AC-20 and a Shell Woodriver AC-5 and AC-20.

Curing rate data at 45°C for the Cosden and Wood River asphalts containing 0.125% manganese (6.25% modifier) and coated 5% on Ottawa sand briquets are shown in Tables 3 and 4, respectively. Selected data displaying the manganese-induced reaction with atmospheric oxygen and the resulting viscosity changes are shown in Figure 5-7 for the Cosden asphalts and in Figures 8-10 for the Wood River asphalts. Changes in ketones, anhydrides, carboxylic acids and sulfoxides were monitored with data reported in the tables. Carboxylic acids were further classified according to the amount of free acid present and the amount of acid complexed with the manganese or otherwise immobilized and unreactive with the analytical reagent used in the determination. Dynamic viscosity measurements at 60°C shown in the tables were determined under near-Newtonian shearing conditions so the data would be comparable.

The ketone and anhydride formation shown in Figures 5-6 and 8-10 for the Cosden and Wood River asphalts demonstrate the rapid reaction of modified asphalts with atmospheric oxygen. As in the earlier studies, unmodified asphalts cured under the same conditions showed the formation of only small amounts of ketones and no anhydrides. As also found in the earlier studies, once the cure is complete, the rate of ketone and anhydride formation in the modified asphalts is greatly reduced. It is noteworthy that most of the ketones formed in the unmodified controls were formed during preparation of the briquets.

Similar amounts of ketones were formed during the cure in both modified AC-5s and AC-20s from the same source, as would be expected; however, total ketones formed were greater in the Cosden than in the Wood River asphalts. Since the same concentration of manganese modifier was used in asphalts from both sources, the differences most likely result from differences in asphalt composition. The anhydride content was lower in the Cosden AC-20 than in the AC-5, probably as a result of the inability of the analytical method, as normally performed, to determine all of the anhydrides present. This is undoubtedly because anhydrides are present in the highly oxidized and strongly associated molecular agglomerates that exist in the benzene solution in which the anhydrides are hydrolyzed for analysis. (As can be seen in Table 3, the viscosity of the cured AC-20 is significantly higher than that of the AC-5, further supporting the presence of more strongly associated micelles in the AC-20.) Any anhydrides not determined in the analysis would contribute to the area of the ketone infrared band, increasing the apparent ketone concentration. If, however, the anhydride content of the AC-20 were adjusted to match that of the AC-5, the apparent ketone content would be reduced by only 0.013 mol. L^{-1}. Thus, the relative ketone concentration is not significantly affected should there be incomplete anhydride hydrolysis. Although anhydride hydrolysis may be incomplete, one may conclude that the manganese-catalyzed reaction has ceased as evidenced by the cessation of a significant increase in either of the interrelated ketone or anhydride concentrations following the initial cure.

One might speculate on the reasons for the differences in relative concentrations of anhydrides and ketones formed on cure as a function of asphalt source. If the manganese is inactivated following cure, as will be discussed in detail in a subsequent section of this report, then one possibility for the relative differences in concentration is that the relative concentration of hydrocarbons that are specific presursors for the anhydrides and stereospecific diketones that inactivate the manganese is greater in the Wood River asphalt than in the Cosden asphalt. Another possibility is that the breakdown of the unstable common hydroperoxide precursors that form the anhydrides and stereospecific diketones favors anhydride formation rather than diketone in the Wood River asphalt. Since the final anhydride concentrations were nearly the same for both Cosden and Wood River asphalts, the former explanation seems most likely. The important conclusion that can be drawn from the data discussed is that the same amount of modifier added to asphalts from different sources can produce different levels of ketone formation, or different levels of cure. The resultant effect on physical properties, however, may be more complex.

In light of the above discussion, it is instructive to compare the viscosity data for the Cosden and Wood River asphalts displayed in Figures 7 and 10, respectively. The relative increase in log viscosities in both of the modified Cosden and Wood River AC-5s after 50 days of cure, as referenced to the corresponding viscosities of the unaged, unmodified AC-5s, is virtually the same, even though the amount of ketone formed in the modified Wood River asphalt was less than that formed in the Cosden asphalt. Thus, the increased sensitivity of the Wood River asphalt to viscosity increase from the formation of ketones was apparently offset by the reduced amount of ketones formed in this asphalt during cure.

A good correlation was found between the rate of formation of ketones and anhydrides and the increase in viscosity as a function of cure time for both modified and unmodified asphalts. As expected, the modified asphalts showed much greater increases in viscosity than the unmodified asphalts, which is an important property imparted by the modification. The rates of viscosity increase following cure are similar for both modified and unmodified asphalts. These data support the conclusion that the manganese has been inactivated and that the time-dependent increase in viscosity after cure is a result of normal, uncatalyzed oxidative aging.

Of practical importance, as previously shown (5), is that the viscosities of the cured AC-5s were lower than the viscosities of the cured AC-20s by an amount roughly equal to the differences in their initial viscosities. Consequently, if a cured product with lower viscosity or stiffness is desired, a modified asphalt with lower initial viscosity may be used.

Some differences, however, were noted between the viscosity increases on cure as a function of asphalt source and grade. The Cosden AC-20 showed about 20% greater sensitivity to viscosity increase during cure than the AC-5, based on the differences between the log viscosities of the unaged, unmodified asphalts and their cured, modified counterparts after 50 days of cure time. This may be further reason to select softer grade asphalts for modification in order to produce cured asphalts with lower final viscosities and potentially reduced sensitivity to low-temperature thermal distress in pavements. The sensitivity to viscosity increase of the Wood River AC-20 after 50 days of cure was only 8% greater than that of the Wood River AC-5.

Thus, the chemical and physical property data on the Cosden and Wood River asphalts show that asphalt composition or source has an influence on the properties of the cured asphalts. Aging studies conducted of unmodified asphalts in the authors' laboratory (15) has similarly shown that the hardening of asphalts from the same level of ketone formation can vary significantly between asphalts of different sources. This variability appears to be closely related to the polar functionality present, its dispersibility, and/or the component compatibility of the asphalt.

Evaluation of the Effects of Modifier Concentration on the Properties of Cured, Modified Asphalts

There were two objectives for the evaluation of the effects of modifier concentration on the properties of the cured asphalt. First, since small amounts of the manganese modifier produce large increases in asphalt viscosity and pavement mixture stiffness, it was important to know the relationship between the viscosity of the cured asphalt and the amount of modifier used. Second, part of the evidence to substantiate the proposed mechanism for the chemical inactivation of the manganese following cure is based on the evaluation of certain chemical functionalities formed in the asphalt as a function of manganese concentration. Thus, a manganese concentration study was needed to evaluate the mechanism.

In the earlier studies using modifier formulation Type 125.3, added 1:9 with asphalt and supplied by Chem-Crete Corporation of Menlo Park, California, a relationship was found between the amounts of anhydrides formed during cure and the amount of manganese present. Data plotted in Figure 11 show that when the modifier concentration was cut in half, only half the anhydrides were formed during the cure with little change in concentration after cure was complete. A relationship between the anhydrides formed during cure and manganese concentration is clearly shown in Figure 12. The plot passes through zero, strongly suggesting a direct or indirect cause and effect relationship between these two parameters. Data in Figure 11 also strongly suggest that there would be a significant ketone concentration associated with the zero manganese concentration.

To examine more completely the relationships between manganese content, anhydrides and ketones formed during cure, and the viscosity of the cured asphalt, Ottawa sand briquets were prepared using the Cosden AC-5 asphalt with manganese contents of 0, 0.05, 0.10, 0.15, 0.20 and 0.25%, and the briquets aged up to 50 days. Compositions containing 0.05 and 0.10% manganese were sampled at 4-, 8-, 20-, and 50-day intervals to monitor progress of the anticipated slower cure to make certain cure was complete for comparative evaluations. Chemical and physical property data on recovered asphalts are shown in Table 5.

Examination of the functional group data show that the cure was complete at 20 days for all modifier concentrations. Although viscosity data were taken after 50 days of cure, the functional group analysis after 20 days of cure was used for subsequent correlations to avoid bias that might be introduced from normal aging of the asphalt after cure was complete. Data on some anhydride determinations were refined by repeating the determination using additions of small amounts of a crown ether to the hydrolysis mixture. The crown ether acts as a sodium-hydroxide phase transfer agent to improve the hydrolysis of anhyrides in the highly oxidized asphalts, as previously discussed. The revised data, shown in parentheses in the table, confirm that incomplete hydrolysis can be a problem. Selected data from Table 5 are plotted in Figures 13-15.

The relationship between anhydrides produced and manganese content (Figure 13) confirms the earlier findings displayed in Figure 12. The anhydride concentration on completion of cure appears directly related to manganese concentration. Although increasing amounts of ketones were found in cured asphalts containing increasing amounts of manganese, as seen in Figure 14, the relationship is not as simple as seen for anhydrides. The plot in Figure 14 strongly suggests that there is a minimum practical lower limit of ketone formation between 0.3 and 0.4 mol. L^{-1} below which one cannot go by reducing manganese content, since there is undoubtedly a lower practical limit of manganese that will give a sufficiently fast rate for the cure. These results have important practical implications with regard to the minimum stiffening of the asphalt that can be affected on cure.

Viscosity data in Figure 15 correlate well with the ketone data in Figure 14 and demonstrate that with the Cosden AC-5 and the present modifier formulation, a minimum practical viscosity for the cured asphalt is about 3x10^4 poise at 60°C when there is a minimum of added manganese. Thus, the minimum viscosity increase on cure is from 5x10^2 to 3x10^4 poise at 60°C, or a viscosity increase of just under two orders of magnitude; and with this asphalt and modifier formulation, cures with a smaller net viscosity increase cannot be practically achieved.

Finally, it is apparent from Figure 15, that manganese concentrations greater than those needed to yield a reasonable cure rate produce relatively small additional increases in viscosity at a cure temperature of 45°C. Data cited earlier in this report show that variations in asphalt source may cause variations in the net increases in viscosity on cure. These variations are equally as great through the range of manganese concentrations evaluated as those seen for the Cosden AC-5 in Figure 15.

One can conclude from the data presented thus far that the change in viscosity on cure is affected by at least three variables: 1) manganese content, 2) initial asphalt viscosity, and 3) variables in asphalt source or composition.

EVIDENCE FOR THE INACTIVATION OF THE MANGANESE FOLLOWING CURE

As mentioned in the introduction, data obtained in an earlier study (5) strongly suggested that the manganese was inactivated following cure and the decrease in rate of change of properties at the end of the cure was not merely a result of the increased viscosity of the system. Data presented in Figures 12 and 13 also suggest a relationship between the amount of anhydrides formed during cure and the amount of manganese present. These results support the mechanism for anhydride formation in asphalt previously proposed by us and illustrated in Figure 3. According to the mechanism, the reaction of aliphatic side chains at the 1,8-positions of the naphthalene ring moiety of asphalt molecules produces an unstable keto-hydroperoxide intermediate that randomly decomposes to form either an anhydride or a stereospecific diketone. It is proposed that the diketone forms complexes with the manganese, causing manganese inactivation. Because either the anhydride or diketone result from a random decomposition product, the concentration of diketones formed should be proportional to the concentration of anhydrides formed, accounting for the direct relationship between anhydrides formed during cure and the amount of manganese present.

Coordinate complexes between manganese (II) and certain beta-diketones and related molecular structures are well known (16-18). Examples, except for the 1,8-naphthalic anhydride, are shown in Figure 16. The bonding forces between the manganese and the organic ligand in these complexes are strong, producing extremely stable adducts. Many of these adducts do not thermally dissociate below their thermal decomposition temperatures. Such coordinate complex formation between the manganese in the Chemkrete product and stereospecific diketones formed during the cure would permanently bond the manganese to the asphalt molecule.

To further understand the chemistry of the manganese inactivation, it was necessary to follow changes in the manganese modifier as the cure proceeded. This was accomplished using previously developed functional group analysis techniques (8-10). Analysis of the manganese modifier is illustrated in Figure 17. Infrared spectra A, B and C (solvent compensated) are spectra of the modifer before treatment and after treatment with triphenyltin hydroxide (TPTH) and sodium hydroxide (NaOH), respectively. The free carboxylic acids in the modifier in access of that needed to complex with the manganese produce the carbonyl absorption band at 1730 cm^{-1} in spectrum A. The carboxyl absorption of the carboxylic acids that are associated with the manganese is shifted to a lower frequency, producing the broad band just below 1600 cm^{-1} in spectrum A. Treatment of the modifier with TPTH, a reagent specific for free carboxylic acids, results in the reaction of only the free acids with the TPTH, eliminating the free acid band at 1730 cm^{-1} (spectrum B) and producing a TPTH-acid complex carbonyl band at about 1640 cm^{-1}. The manganese-carboxylic acid complex is virtually undisturbed by the TPTH. Finally, reactions of a separate sample of manganese modifier with NaOH converts all carboxylic acids, whether free or manganese-complexed, to carboxylate salts, eliminating virtually all carboxyl absorption (spectrum C). The virtual absence of a carboxylate salt absorption below 1600 cm^{-1} undoubtedly results from the insolubility of these salts in the spectral solvent.

Differential spectra are used to quantitatively follow the amounts of free acids and manganese-complexed acids in the asphalt during cure. These spectra are illustrated for the modifier analysis in Figure 17. If a differential spectra of the TPTH-treated sample versus the untreated sample is obtained, all absorption bands that are unaltered by the TPTH are nulled and only the free acid band appears. The area of this band is directly related to concentration of free carboxylic acids. For quantification of total free and manganese-complexed acids, the sample is reacted with a silylation mixture of hexamethyldisilyzane (HMDS) and trimethylchlorosilane (TMCS) that converts all carboxylic acids or acid salts to their silyl esters with a carboxyl absorption band at 1715 cm^{-1} (Figure 17). The area of this band under the differential spectra for the untreated, silylated versus the TPTH-treated samples is directly related to the total carboxylic acid content of the spectra. The amount of carboxylic acids complexed with the manganese is thus the difference between the amounts calculated as free acids and total acids.

To confirm the ability of the manganese in the asphalt modifier formulation to form coordinate complexes with diketones, a sample of the modifier was mixed with a diketone (dibenzoylmethane) known to form coordinate complexes with manganese (II). Dibenzoylmethane forms a coordinate of the type illustrated for acetonylacetone (Figure 16) in which three molecules of the diketone are attached to the manganese through their six carboxyl oxygens. Spectra confirming the coordination complex reaction are shown in Figure 18. The spectrum of the mixture clearly shows the doublet absorption bands at about 1540 and 1590 cm^{-1} for the carbonyl forming the coordinate bond with the manganese. A significant increase occurs in the free acid band at 1730 cm^{-1} in the mixture as the carboxylic acids that were initially complexed with the manganese are displaced from the manganese by coordinate complex formation with the dibenzoylmethane. Further confirmation for the destruction of the initial carboxylic acid-manganese complex is evidenced by the loss of the band characteristic of this complex (broad band just below 1600 cm^{-1}) in the spectrum of the mixture. The appearance of additional free acids in the spectra during cure is used in experiments described later as evidence of manganese-diketone coordinate complex formation.

Because of the correlation found between anhydrides formed on cure and the manganese content of the modified asphalt, it was important to determine whether or not the anhydride participated in the manganese inactivation. To answer this question, modified AC-5 asphalt B-3037 was spiked with 0.2 mol. L^{-1} concentrations of either the diketone, dibenzoylmethane, or 1,8-naphthalic anhydride (the type formed in asphalt on oxidative aging [13]). The spiked asphalts were coated on Ottawa sand and air-aged in briquets at 45°C. The briquets were sampled as a function of time, the asphalts extracted, and ketone and carboxylic acid contents determined. Results of the analyses are shown in Figure 19. The cure was virtually complete, as indicated by ketone formation, during the first few days of aging in the sample containing the anhydride. Thus, the anhydride appeared to have little, if any, effect on reducing the catalytic activity of the manganese. The rate of ketone formation in the sample containing the diketone spike, however, was greatly reduced, indicating that the activity of the manganese had been inhibited by the diketone. Since dibenzoyl methane is itself highly sensitive to air oxidation (contains similar benzylic functionality responsible for ketone formation in asphalt), much of the ketone functionality formed later on in the diketone-spiked sample probably resulted from dibenzoylmethane oxidation. Evidence for this was obtained when 50-day-aged briquets (data not shown) showed considerably higher ketone content in the dibenzoylmethane-spiked sample than in the sample spiked with anhydride. Further confirmation that the added diketone participated in coordinate complex formation and that the added anhydride did not is evidenced by the liberation of free carboxylic acids (0.3 to 0.5 mol. L^{-1}) upon addition of the diketone whereas there was no liberation of free acids from the manganese modifier on addition of the anhydride (Figure 19). Also, no additional acids were liberated from the diketone-spiked sample during cure. In conclusion, this experiment shows that diketones capable of forming coordinate complexes with manganese inhibit the catalytic activity of the manganese modifier in asphalt, and anhydrides of the type formed in asphalt on oxidative aging do not.

To examine the relationship between carboxylic acids liberated from the manganese-acid complex of the modifier and the formation of the coordinate complex of manganese with stereospecific diketone, dibenzoylmethane was added to a solution of Type 150.40 manganese modifier supplied by Chem-Crete Corporation of Menlo Park, California. Increments of dibenzoylmethane sufficient to form 1:1, 2:1, and 3:1

complexes with manganese (a 3:1 complex is illustrated for acetonylacetone in Figure 16) were sequentially added (based on sample weight, purity not known) and the free acids liberated together with the corresponding coordinate complex formed were monitored by infrared spectrometry. Results are plotted in Figure 20. A good correspondence between the acids liberated and the complex formed is seen until 2 moles of dibenzoylmethane per mole of manganese, sufficient to form the 2:1 complex, had been added. The correspondence between acids liberated and dibenzoylmethane added is not mole for mole; however, the near straight-line relationship suggests that the discrepancy probably resulted largely from impure dibenzoyl methane. A 20% impurity could account for the discrepancy. Thus, it appears that for each diketone molecule added that coordinates with the manganese, one carboxylic acid molecule is liberated until the 2:1 complex is formed. The data indicate that the third molecule for diketone added to form the 3:1 complex coordinate with the manganese does not liberate carboxylic acid. These results suggest a +2 valence state for manganese associated with two molecules of carboxylic acid in the initial modifier formulation, and that these acids are liberated during the reaction of manganese with the first two moles of diketone in coordinate complex formation.

To compare the chemistry of the asphalt cure with the reactions that occurred during reaction of modifier with dibenzoylmethane, the actual acids liberated during the cure of AC-5 asphalt B-3037 modified with Type 150.40 formulation were compared with the acids liberated in the dibenzoylmethane-modifier reaction. Functional group analysis showed that 0.6 mol. L^{-1} of carboxylic acid had been liberated from the modifier formulation after the proposed 2:1 complex had been formed. Had this reaction with the modifier occurred at its normal concentration of 1:15 in a modified asphalt, the equivalent concentration of acids liberated would have been 0.038 mol. L^{-1} ($0.6 \div 16$). However, the actual amount of acids found liberated when cure was complete for the modified AC-5 was just half this amount, or 0.18 mol. L^{-1}. These results suggest that when the cure is complete at this temperature only one stereospecific diketone from asphalt is coordinated with one manganese atom, forming a 1:1 rather than a 2:1 complex with at least one acid molecule still remaining with the manganese.

A final experiment was designed to carefully follow the curing reaction, particularly during the early stages of the reaction. The CTI-101™ modifier from current production of Chemkrete Technologies, Inc. was used. The Cosden AC-5 asphalt modified with 0.125% manganese (6.25% modifier) was deposited on Ottawa sand from benzene solution to avoid reaction with atmospheric oxygen during briquet preparation as described in the experimental section. Briquets were cured as a function of time at 45°C. Functional group analyses as a function of cure time on extracted asphalts are shown in Table 6 and Figure 21.

Data collected during the first 24 hours of cure at 45°C are shown at the left side of Figure 21. The concentration of free and complexed acids remained constant during the first 24-hour period, indicating no change in the manganese-carboxylic acid complex, and thus no change in its catalytic activity. Ketones, however, showed a rapid increase to about 0.2 mol. L^{-1} during the first 24 hours, thus verifying the activity of the manganese modifier. Also, as expected, no anhydrides were formed during the first 24 hours, demonstrating the inhibition period for anhydride formation previously discussed.

The sampling at two days showed changes beginning to take place in all the functionalities. Anhydrides were beginning to form at a ketone content of between 0.3 and 0.4 mol. L^{-1} as predicted from Figures 2, 3, and 14. Based on the proposed simultaneous formation of anhydrides and stereospecific bridgehead diketones, the concentration of manganese-complexed carboxylic acids should begin to decrease with a corresponding increase in free acids as the acids are liberated during the formation of the manganese coordinate complex with the stereospecific diketone. This appears to have occurred. These changes continued with cure time, reaching their final stabilized state after about 20 days. (Complete cure took about 20 days rather than the 2-4 days required for briquets prepared hot because part of the cure occurs during hot briquet preparation at 150°C.) After 20 days, the manganese was inactivated and the rapid formation ketones and anhydrides ceased. The expected cessation in changes in free and complexed acids also occurred.

Although the experimental results strongly indicate that the manganese forms a coordinate complex with the 1,8-bridgehead diketone formed simultaneously with anhydrides, one cannot rule out the possibility that diketones formed at adjacent positions on aromatic ring systems do not also form coordinate complexes with manganese. In fact, it is highly probable that they do. However, since their appearance should be delayed in the oxidation process as is the appearance of anhydride and 1,8-bridgehead diketone, their participation in the manganese inactivation would probably not be detected by the experiments conducted. Their effect on manganese inactivation should be similar to that of the 1,8-bridgehead diketone.

Based on the smoothed data from the plot in Figure 21, the concentration of the manganese-complexed acids changed during cure from about 0.038 to 0.016 mol. L^{-1}, or about 0.022 mol. L^{-1}. Assuming the removal, on the average, of only one mole of acid per mole of manganese as previously suggested, this change corresponds to the loss of 0.12% manganese from the acid complex to its inactivated diketone complex (0.22 mol/L x 55 g/mol = 1.2 g/L, or 0.12% based on a density of one for asphalt). This percentage is in good agreement with the actual content of manganese (0.125%) in the modified asphalt. Assuming two carboxylic acids to be complexed with the manganese in the initial manganese modifier (manganese in the +2 valence state), the calculations indicate that approximately one carboxylic acid molecule remains still complexed with the manganese in its inactivated form, as suggested from the earlier experiment.

A possible reason that one molecule of acid remains with the manganese following cure is that following the reaction between the manganese and the asphalt diketone, the diketone complex, together with its remaining complexed acid, is occluded within an agglomerate or micelle of polar asphalt molecules. Current models for the physical state of asphalt consider the highly polar components to be associated into micellar bodies that are dispersed in the asphalt matrix. This occlusion would thus prevent the further reaction of the manganese with the additional potential diketone-coordinating sites on the manganese atom. If the manganese forms a 1:1 complex with asphalt diketone, then the manganese may not act as a "cross linking" agent, as previously suggested (2), to link asphalt components together, but becomes a rather inert part of a molecular agglomerate. This factor would explain the similar properties found (5) between cured, modified asphalt and a corresponding unmodified asphalt aged in the laboratory to the same ketone content.

If the above analysis has basis in fact, the effect of temperature on the curing reaction and in turn the properties of the cured product needs to be addressed. Increasing temperature reduces molecular structuring or association in asphalt, and thus may possibly cause sufficient micelle dissociation to allow two diketones from two different asphalt molecules to complex with one manganese atom during the cure. This could have a "cross linking" effect and possibly produce changes in physical properties of the cured asphalt not seen in products cured at a lower temperature. Also, based on the proposition that the 1:1 manganese-asphalt complex is occluded in an asphalt micelle, the question still remains as to whether the 1:1 complex is still catalytically active, and whether it would again promote rapid reaction with atmospheric oxygen if liberated by micellar dissociation on increasing temperature.

CONCLUSIONS

The following statements summarize the important conclusions drawn from this investigation:

1. The manganese modifier promotes a rapid reaction of asphalt with atmospheric oxygen during the cure to produce a corresponding rapid increase in viscosity.

2. After a certain level of manganese-induced reaction has been achieved, the rapid reaction ceases. Further reaction with atmospheric oxygen is characteristic of normal air aging.

3. The cure ceases when a given amount of oxidation has occurred, the amount being determined by the oxidation chemistry of the asphalt.

4. Because the incremental increase in viscosity on cure results from the incremental amount of oxidation on cure, softer asphalts produce less stiff cured products.

5. There is a minimum practical lower limit of incremental increase in viscosity on cure. With the asphalts studied this was between one and one-half and two orders of magnitude.

6. The incremental increase in viscosity on cure is influenced to some degree by both manganese content and asphalt source.

7. Strong evidence was obtained to show that following cure, the manganese is inactivated by forming a coordinate complex with stereospecific diketones formed in the asphalt during cure. Thus, the rate of formation of the diketones is the controlling factor that determines the amount of change on cure.

8. Evidence for the inactivation of manganese by the diketone provided confirmation for the mechanism of anhydride formation in asphalts. According to the mechanism, anhydrides are formed simultaneously with the stereospecific diketone from a common intermediate hydrocarbon oxidation product in asphalt containing keto-hydroperoxide functionality.

9. The manganese apparently forms a 1:1 coordinate complex with diketones at the 45°C cure temperature used. It is suggested that the coordinate complex, with at least one remaining complexed carboxylic acid, becomes occluded in an agglomerate of asphalt molecules, and does not become significantly involved in crosslinking reactions between micellar asphalt components.

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Table 1. Chemical Functional Groups Formed During Curing of Modified and Unmodified Asphalts

Cured(1) time, days	Concentration, mol. L^{-1}					
			Carboxylic acids			
	Ketones	Anhydrides	Free	Complexed(2)	Total	Sulfoxides
			AC-5 (B-3037), Unmodified			
0	0	0	Trace	0	Trace	Trace
2	0.03	0	Trace	0	Trace	0.17
4	0.06	0	Trace	0	Trace	0.18
8	0.10	0	Trace	0	Trace	0.18
20	0.10	0	Trace	0	Trace	0.18
50	0.10	0	Trace	0	Trace	0.21
210	0.15	0	Trace	0	Trace	0.21
			AC-5 (B-3037), Modified(3)			
0	0	0	0.013	0.052	0.065	Trace
2	0.43	0.022	0.025	--	--	0.28
4	0.46	0.030	0.030	0.035	0.065	0.29
8	0.46	0.024	0.028	0.028	0.055	0.30
20	0.42	0.031	0.028	0.035	0.063	0.27
50	0.47	0.027	0.033	0.032	0.065	0.24
210	0.50	0.035	0.033	0.032	0.065	0.22
			AC-20 (B-3035), Unmodified			
0	0	0	Trace	0	Trace	Trace
2	0.05	0	Trace	0	Trace	0.16
4	0.06	0	Trace	0	Trace	0.17
8	0.08	0	Trace	0	Trace	0.18
20	0.08	0	Trace	0	Trace	0.20
50	0.11	0	Trace	0	Trace	0.23
210	0.14	0	Trace	0	Trace	0.23
			AC-20 (B-3035), Modified(3)			
0	0	0	0.013	0.052	0.065	Trace
2	0.35	0.019	0.021	0.043	0.064	0.29
4	0.39	0.026	0.028	0.035	0.063	0.25
8	0.51	0.027	0.032	0.031	0.063	0.26
20	0.52	0.030	0.032	0.029	0.061	0.30
50	0.50	0.026	0.032	0.029	0.061	0.25
210	0.57	0.028	0.033	0.030	0.063	0.22

(1) Cured at 45°C in 50-g briquets prepared from 5% by weight asphalt coated on Ottawa sand
(2) Acids complexed with manganese, obtained by difference
(3) Modified asphalt contained 0.14 weight percent active manganese

Table 2. Changes in Viscosity and Ketone Concentration During Aging at Curing Temperature of 45°C

Aging time, days	Modifier/ asphalt ratio	Active(1) manganese, %	Dynamic viscosity, poise, 60°C, 0.1 rad/s (ketones, mol.L^{-1})							
			AC-5 asphalt, B-3037				AC-20 Asphalt, B-3035			
			Unmodified		Modified		Unmodified		Modified	
None	1:9	0.17	9.37×10^{2}	(0.0)	4.30×10^{2}	(0.0)	5.25×10^{3}	(0.0)	1.97×10^{3}	(0.0)
50	1:9	0.17	--	(---)	4.38×10^{4}	(0.49)	--	(---)	1.83×10^{5}	(0.51)
None	1:15	0.14	9.70×10^{2}	(0.0)	5.54×10^{2}	(0.0	4.59×10^{3}	(0.0)	2.03×10^{3}	(0.0)
50	1:15	0.14	2.02×10^{3}	(0.10)	2.45×10^{4}	(0.47)	1.23×10^{4}	(0.11)	7.70×10^{4}	(0.50)
210	1:15	0.14	3.07×10^{3}	(0.15)	1.12×10^{5}	(0.50)	1.73×10^{4}	(0.14)	3.50×10^{5}	(0.57)

1) Active manganese was estimated by infrared analysis of complexed carboxylic acids. Nominal manganese content, based on reported manganese content of modifier, would be 0.20 and 0.125% for modifier/asphalt ratio of 1:9 and 1:15, respectively.

Table 3. Curing Rate Data on Manganese-Modified Cosden Asphalt

Cure time[1] days	Concentration, mol. L^{-1}						Dynamic viscosity, poise, 60°C, 0.01 r/s
			Carboxylic acids[2]				
	Ketones	Anhydrides	Free	Complexed	Total	Sulfoxides	
			AC-5, Unmodified				
Original	0	0	Trace	0	Trace	Trace	5.1×10^2
After coating	0	0	Trace	0	Trace	0.025	--
1	0.07	0	0.003	0	Trace	0.022	--
2	0.06	0	0.003	0	Trace	0.022	--
4	0.06	0	Trace	0	Trace	0.022	--
8	0.06	0	Trace	0	Trace	0.029	1.3×10^3
20	0.09	0	Trace	0	Trace	0.091	1.8×10^3
50	0.11	0	0.008	0	0.008	0.20	2.3×10^3
100	0.11	0	0.014	0	0.014	0.20	3.3×10^3
			AC-5, Modified				
Original	0.05	0	0.010	0.038	0.048	Trace	2.8×10^2
After coating	0.09	( )[3]	0.012	0.032	0.044	0.033	--
1	0.22	( )[3]	0.012	0.028	0.040	0.14	--
2	0.36	0.009	0.014	0.026	0.040	0.18	--
4	0.37	0.021	0.033	0.020	0.053	0.21	--
8	0.38	0.035	0.033	0.020	0.053	0.21	3.5×10^4
20	0.44	0.036	0.040	0.016	0.056	0.22	3.7×10^4
50	0.41	0.040	0.039	0.024	0.063	0.21	4.3×10^4
100	0.43	0.040	0.040	0.023	0.063	0.22	7.2×10^4
			AC-20, Unmodified				
Original	0	0	Trace	0	Trace	Trace	1.72×10^3
After coating	0.03	0	Trace	0	Trace	0.022	--
1	0.06	0	0.017(?)	0	0.017	0.018	--
2	0.05	0	Trace	0	Trace	0.029	--
4	0.08	0	Trace	0.035(?)	0.035	0.069	--
8	0.09	0	Trace	0	Trace	0.061	5.60×10^3
20	0.12	0	Trace	0	Trace	0.15	7.25×10^3
50	0.11	0	Trace	0	Trace	0.20	1.02×10^4
100	0.12	0	Trace	0	Trace	0.19	1.64×10^4
			AC-20, Modified				
Original	0.03	0	0.007	0.043	0.050	Trace	6.0×10^2
After coating	0.24	( )[3]	0.009	0.025	0.034	0.076	--
1	0.33	( )[3]	0.021	0.021	0.042	0.16	--
2	0.38	0.015	0.030	0.046	0.076	0.18	--
4	0.39	0.030	0.032	0.029	0.061	0.21	--
8	0.39	0.031	0.035	0.026	0.061	0.21	2.09×10^5
20	0.40	0.032	0.045	0.022	0.067	0.21	3.02×10^5
50	0.43	0.035	0.045	0.026	0.071	0.20	5.80×10^5
100	0.46	0.037	0.042	0.021	0.063	0.21	6.95×10^5

[1] Cured as 5% coating on Ottawa sand briquets in air at 45°C

[2] Acids complexed with manganese, obtained by difference

[3] Some unknown hydrolyzable material (probably not anhydrides); broad band centered at 1715 cm^{-1}, equivalent in area to 0.004 to 0.007 mol. L^{-1} anhydrides

Table 4. Curing Rate Data on Manganese-Modified Wood River Asphalt

Cure time[1] days	Concentration, mol. L^{-1}						Dynamic viscosity, poise, 60°C, 0.01 r/s
			Carboxyolic acids				
	Ketones	Anhydrides	Free	Complexed[2]	Total	Sulfoxides	
AC-5, Unmodified							
Original	0	0	0	0	0	Trace	6.2 x 10^2
After coating	0.05	0	0	0	0	Trace	--
1	0.04	0	0	0	0	0.05	--
2	0.06	0	0	0	0	0.08	--
4	0.05	0	0	0	0	0.11	--
8	0.06	0	0	0	0	0.12	1.4 x 10^3
20	0.075	0	0	0	0	0.15	1.8 x 10^3
50	0.09	0	0	0	0	0.18	2.7 x 10^3
100	0.09	0	Trace	0	Trace	0.18	3.2 x 10^3
AC-5, Modified							
Original	0.02	0	()[3]	()[3]	0.055	0.065	3.0 x 10^2
After coating	0.7	0	0.23	0.025	0.048	0.05	--
1	0.12	0	--	--	0.059	0.13	--
2	0.26	0.008	0.14	0.018	0.032	0.22	--
4	0.24	0.023	0.023	0.017	0.040	0.26	--
8	0.31	0.034	0.021	0.021	0.042	0.027	4.0 x 10^4
20	0.34	0.036	0.038	0.019	0.057	0.029	4.8 x 10^4
50	0.37	0.044	0.044	0.017	0.060	0.32	6.6 x 10^4
100	0.35	0.034	0.033	0.022	0.055	0.27	1.0 x 10^5
AC-20, Unmodified							
Original	0	0	0	0	0	Trace	1.95 x 10^3
After coating	0.05	0	0	0	0	0.3	--
1	0.05	0	0	0	0	0.04	--
2	0.06	0	0	0	0	0.07	--
4	0.05	0	0	0	0	0.09	--
8	0.06	0	0	0	0	0.10	6.0 x 10^3
20	0.07	0	0	0	0	0.13	7.8 x 10^3
50	0.09	0	0	0	0	0.18	1.0 x 10^4
100	0.08	0	Trace	0	Trace	0.18	1.21 x 10^4
AC-20, Modified							
Original	0.05	0	0.014[4]	0.037	0.051	0.09	4.07 x 10^2
After coating	0.10	0	0.014	0.039	0.053	0.05	--
1	0.12	0	0.014	0.034	0.048	0.16	--
2	0.28	0.006	0.018	0.030	0.048	0.26	--
4	0.32	0.013	0.025	0.025	0.050	0.30	--
8	0.33	0.32	0.051	0.023	0.074	0.32	1.39 x 10^5
20	0.34	0.033	0.038	0.023	0.061	0.29	2.10 x 10^5
50	0.33	0.038	0.034	0.022	0.056	0.32	2.85 x 10^5
100	0.34	0.037	0.025	0.021	0.046	0.27	5.23 x 10^5

1 Cured as 5% coating on Ottawa sand briquets in air at 45°C
2 Acids complexed with manganese, obtained by difference
3 Absorption in 1700 cm^{-1} region which is reactive with TPTH interferes with the acid determination
4 Correction made for unknown acidic absorption in 1700 cm^{-1} region

Table 5. Properties of Cured[1], Modified Cosden AC-5 Asphalt as a Function of Modifier Concentration

Manganese, percent	Cure time, days	Concentration, mol. L^{-1}						Viscosity,[3] poise, 60°C, 0.01 r/s
				Carboxylic acids				
		Ketones	Anhydrides	Free	Complexed[2]	Total	Sulfoxides	
0	0	<0.05	0	Trace	0	Trace	Trace	5.1×10^2
0.05	4	0.25	0.014	0.014	0.007	0.021	0.24	
0.05	20	0.31 (0.38)[4]	0.025 (0.013)[4]	0.018	0.011	0.029	0.27	
0.05	50	0.33	0.023	0.019	0.006	0.026	0.25	2.9×10^4
0.10	4	0.33	0.032	0.016	0.009	0.025	0.23	
0.10	8	0.35	0.038	0.028	0.016	0.044	0.22	
0.10	20	0.38 (0.42)	0.035 (0.028)	0.036	0.018	0.054	0.22	
0.10	50	0.40	0.040	0.036	0.025	0.061	0.22	
0.15	20	0.45[5] (0.43)	0.041[5] (0.039)	0.044	0.031	0.075	0.23	
0.15	50	--	--	--	--	--	--	5.2×10^4
0.20	20	0.47 (0.46)	0.049 (0.051)	0.056	0.052	0.108	0.21	
0.20	50	--	--	--	--	--	--	6.1×10^4
0.25	20	0.48 (0.47)	0.052 (0.062)	0.063	0.055	0.118	0.20	
0.25	50	--	--	--	--	--	--	7.1×10^4

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[1] Ottawa sand briquets coated with 5% asphalt and cured at 45°C in air

[2] By difference

[3] Dynamic viscosity at shear rate shown to be near Newtonian behavior

[4] Revised values obtained using crown ether in anhydride hydrolysis step during analysis

[5] Ketones and anhydrides adjusted from 0.46 and 0.035 mol. L^{-1}, respectively, because of incomplete anhydride hydrolysis (based on infrared band area, 0.225 mol. L^{-1} anhydride is equivalent to 1.0 mol. L^{-1} ketone)

Table 6. Kinetic Data and Functional Group Changes During Curing of Manganese-Modified Cosden AC-5 Asphalt

	Concentration, mol. L^{-1}				
			Carboxylic Acids		
Cure time	Ketones	Anhydrides	Free	Complexed(1)	Total
None	0.01	0	0.009	0.039	0.048
2 hours	0.01	1	0.015	0.037	0.052
4 hours	0.025	0	0.019	0.035	0.054
8 hours	0.04	0	0.014	0.040	0.054
16 hours	0.08	0	0.016	0.032	0.048
24 hours	0.08	0	0.012	0.038	0.050
2 day	0.17	0.004	0.017	0.033	0.050
4 day	0.28	0.028	0.025	0.034	0.059
8 day	0.36	0.041	0.033	0.025	0.058
20 day	0.40	0.041	0.042	0.010	0.052
50 day	0.43	0.043	0.041	0.018	0.059
100 day	0.42	0.037	0.041	0.022	0.063

(1) Obtained by difference

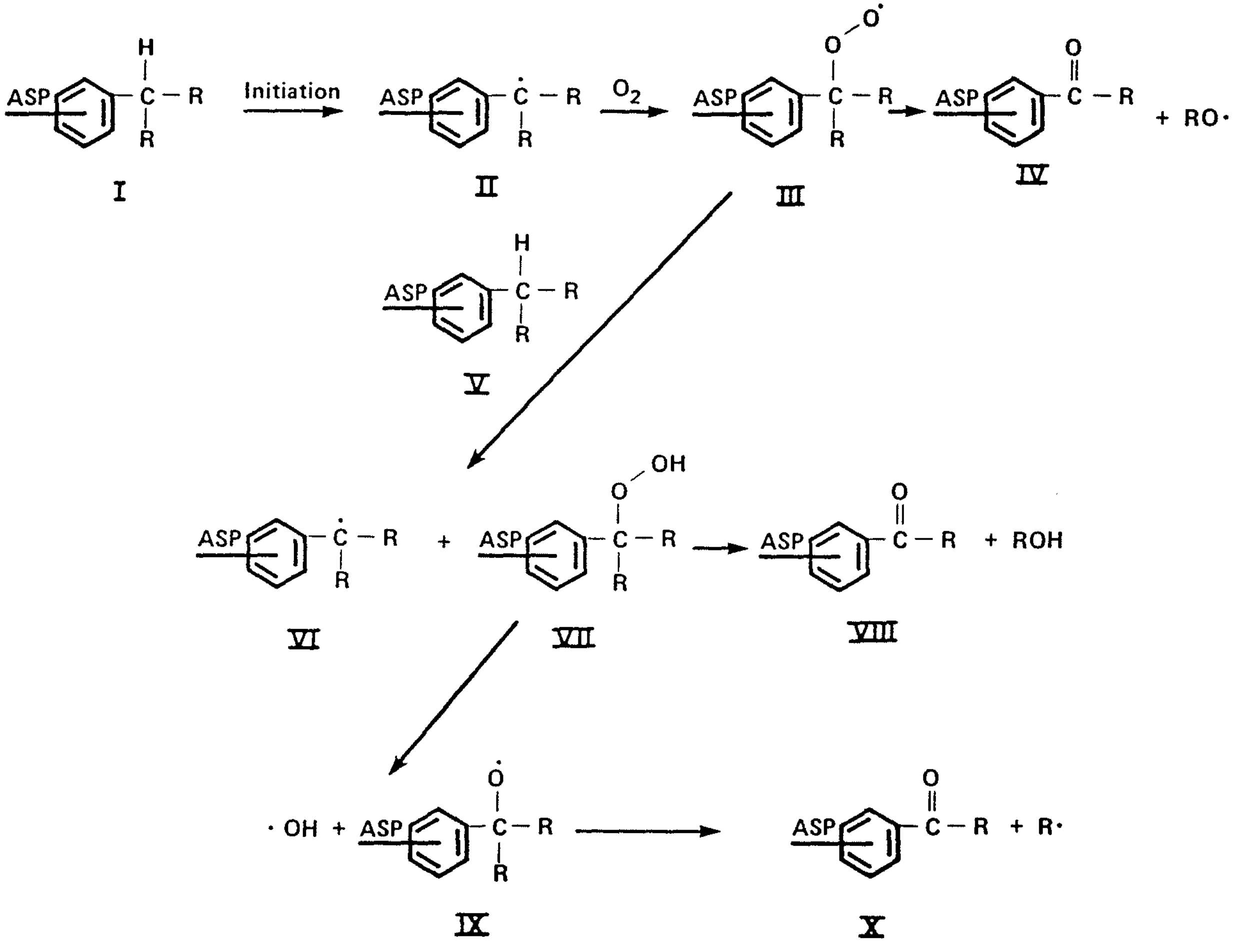


Figure 1. A Suggested Mechanism for the Free Radical Air Oxidation of Asphalt

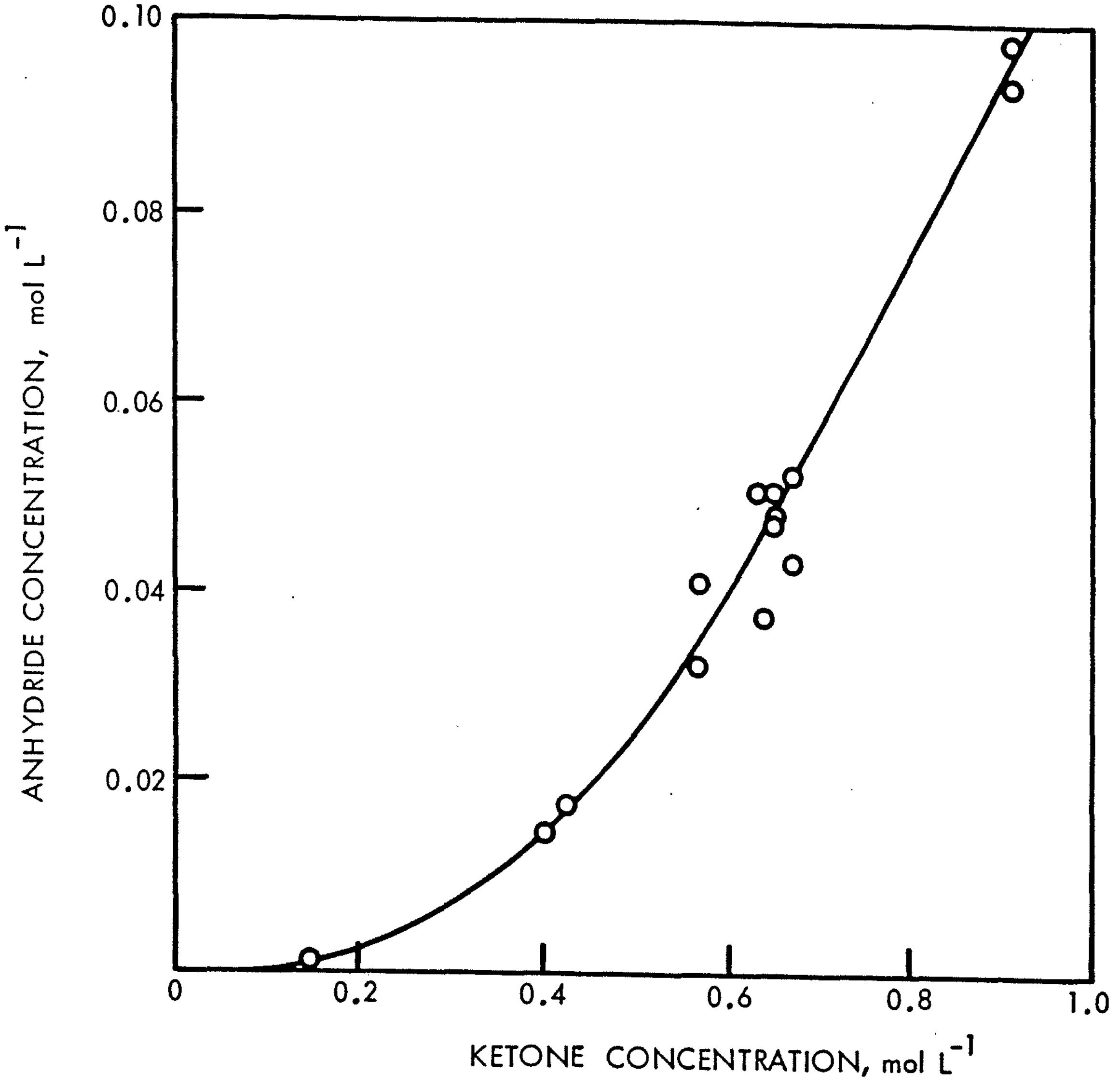


Figure 2. Relationship of Anhydrides to Ketones Formed in Asphalt as a Function of Level of Oxidation

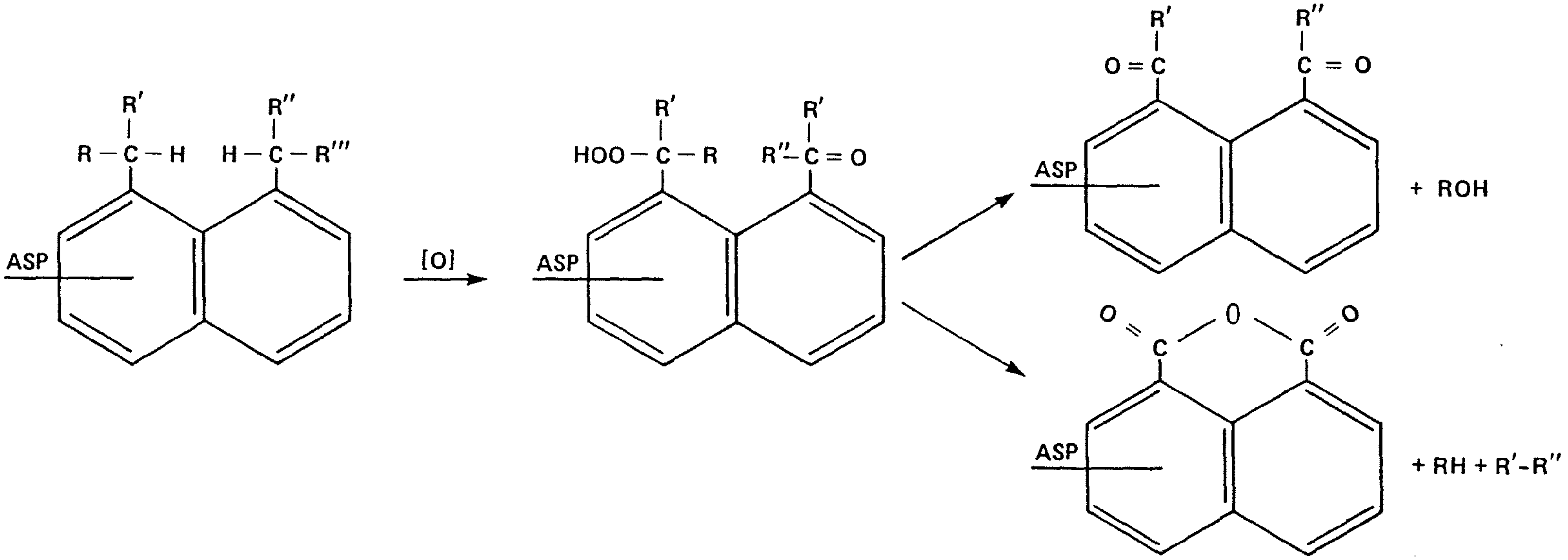


Figure 3. Proposed Mechanism for the Formation of Anhydrides and Stereospecific Diketones in Asphalt on Oxidation

MANGANESE CONTENT: 0.125 PERCENT

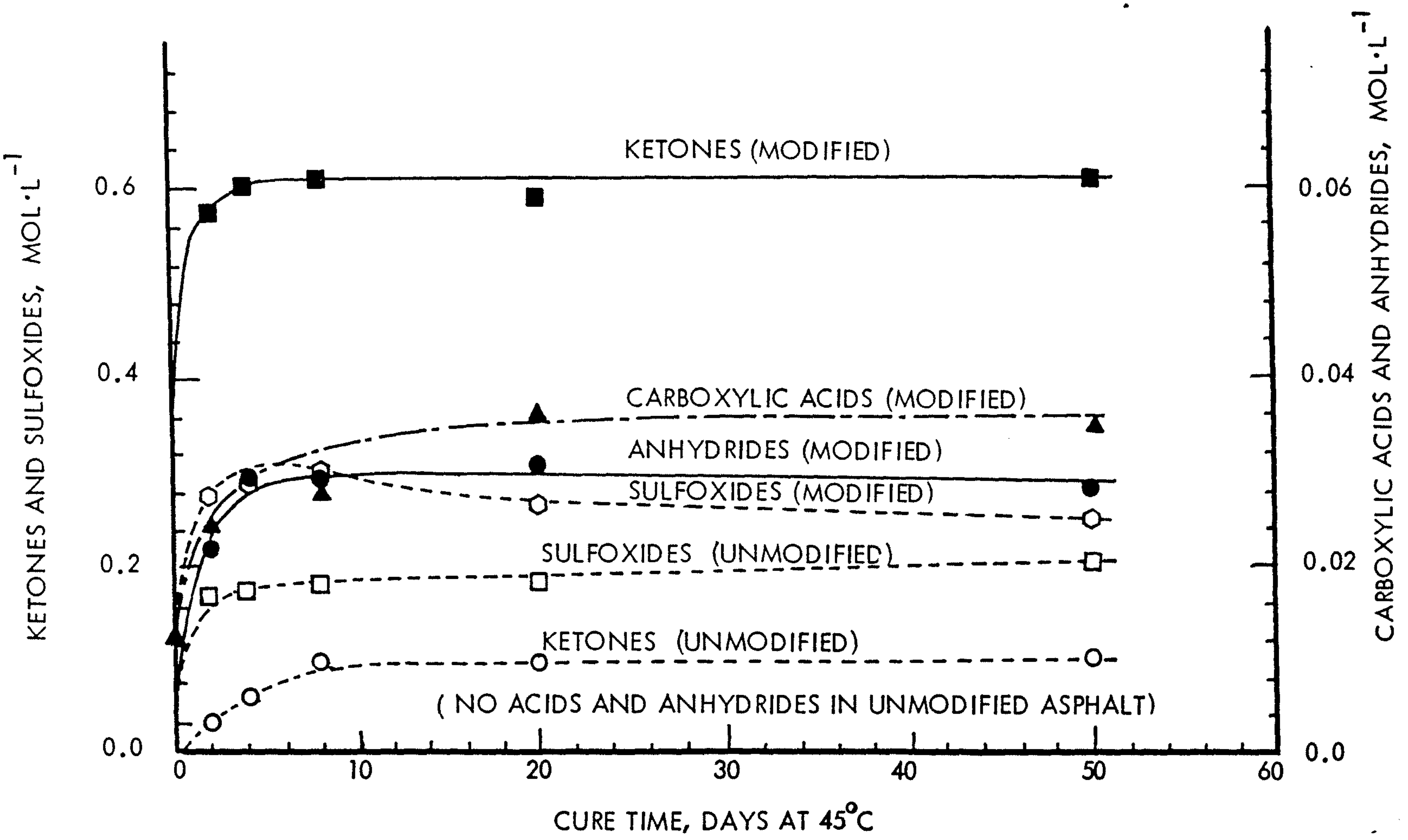


Figure 4. Chemical Functional Groups Formed as a Function of Cure Time in Modified and Unmodified AC-5 Asphalt

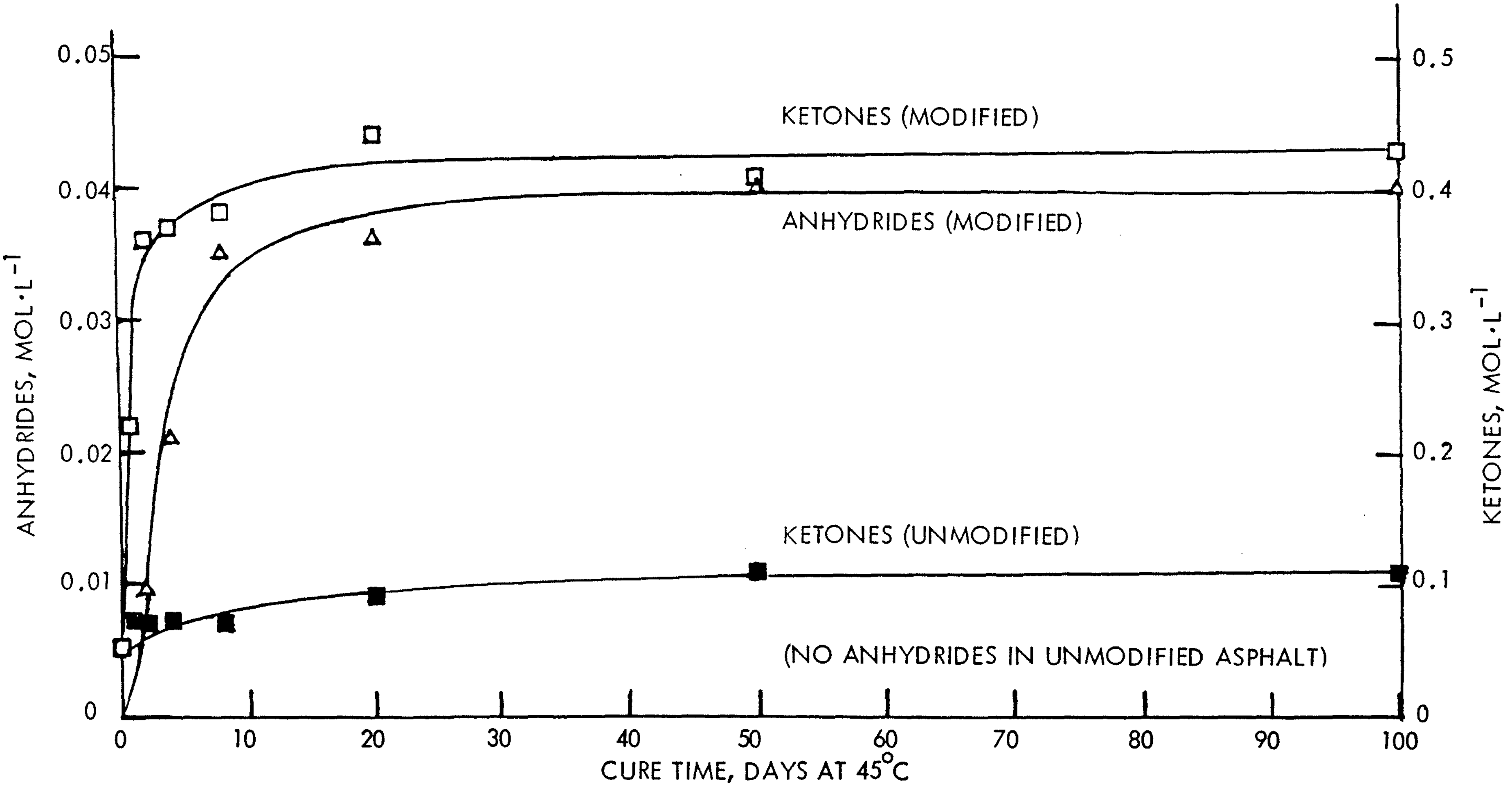


Figure 5. Ketone and Anhydride Formation During Cure of Manganese-Modified and Unmodified Cosden AC-5 Asphalt

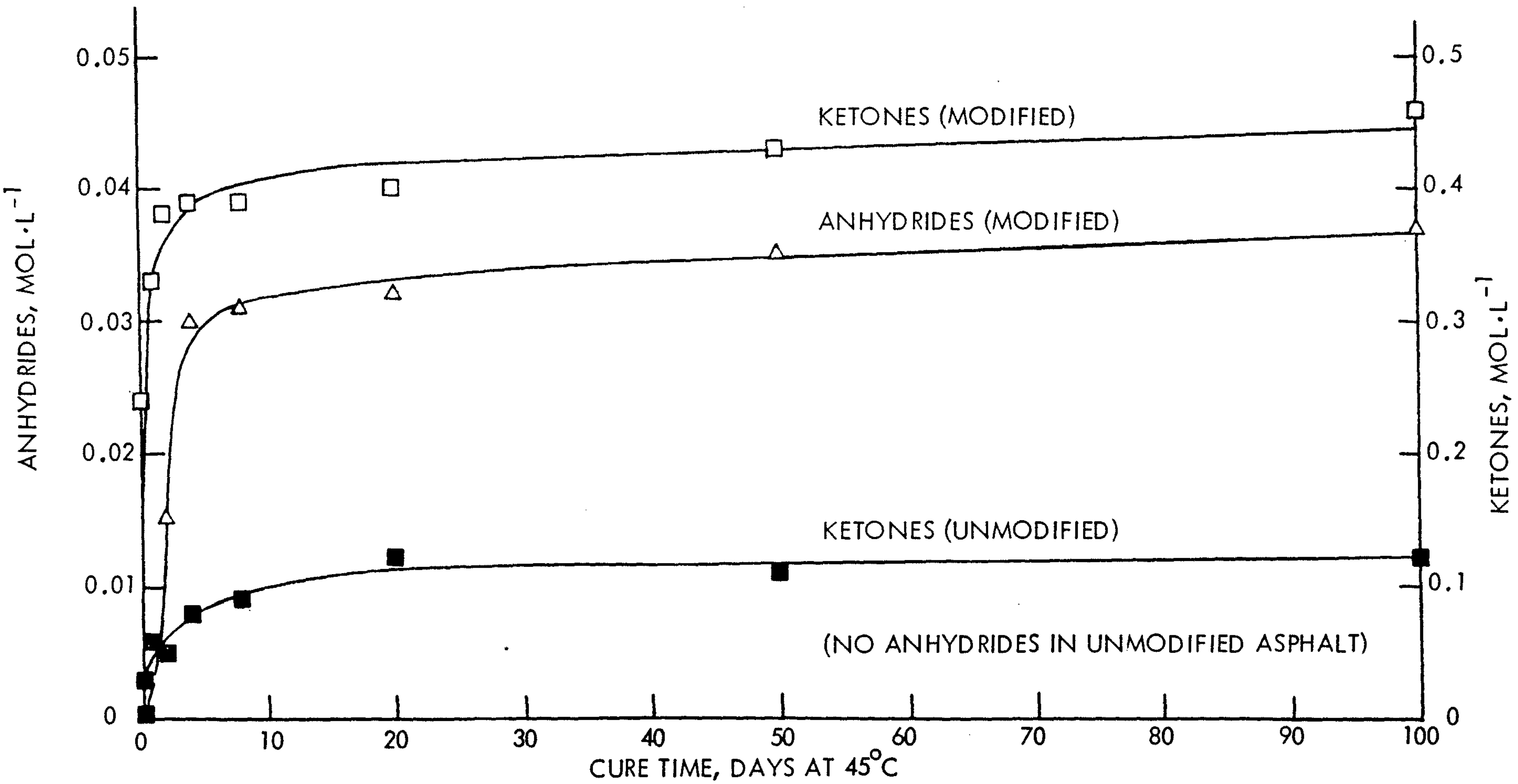


Figure 6. Ketone and Anhydride Formation During Cure of Manganese-Modified and Unmodified Cosden AC-20 Asphalt

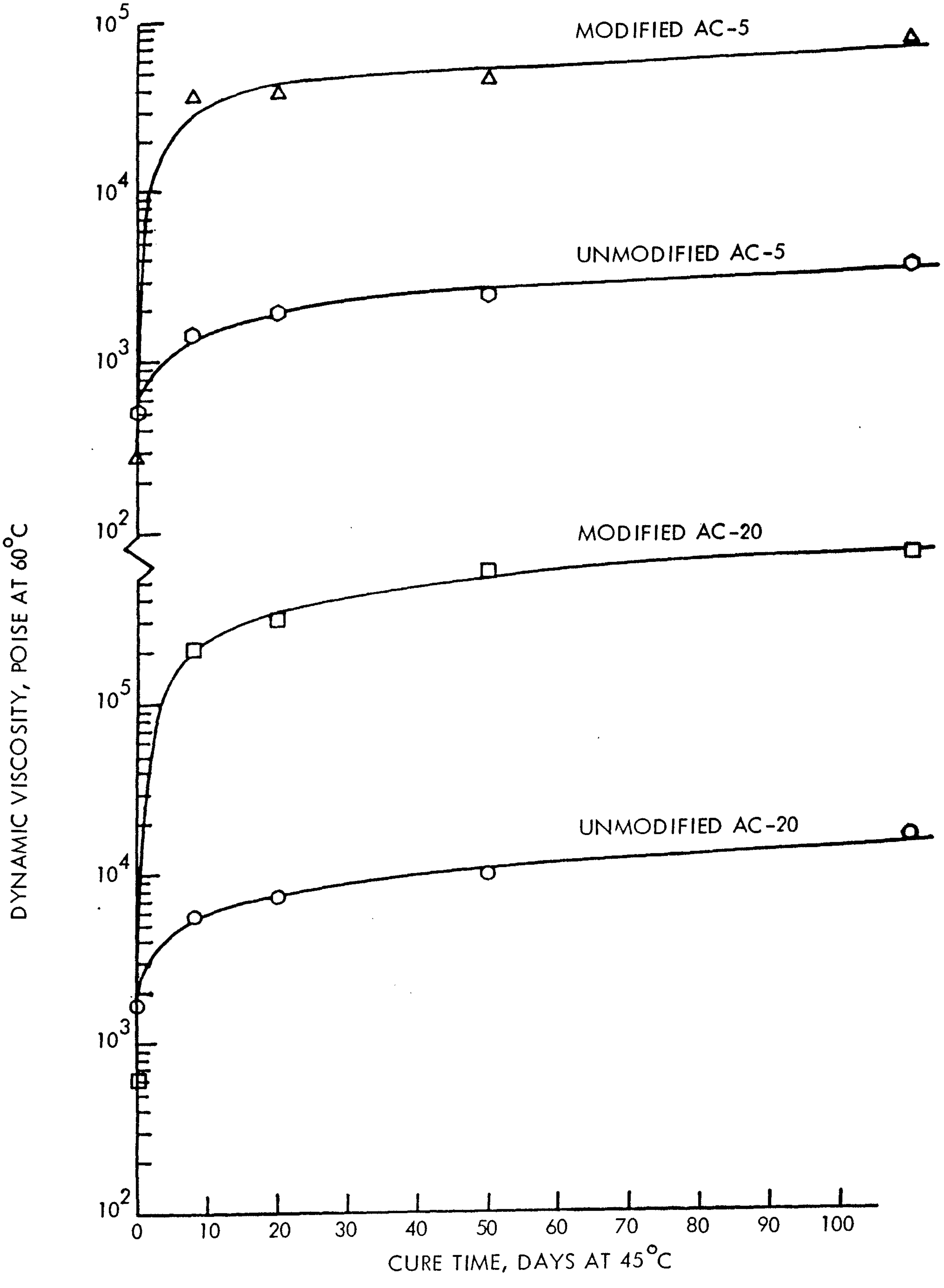


Figure 7. Change in Viscosity During Cure of Manganese-Modified and Unmodified Cosden AC-5 and AC-20 Asphalts

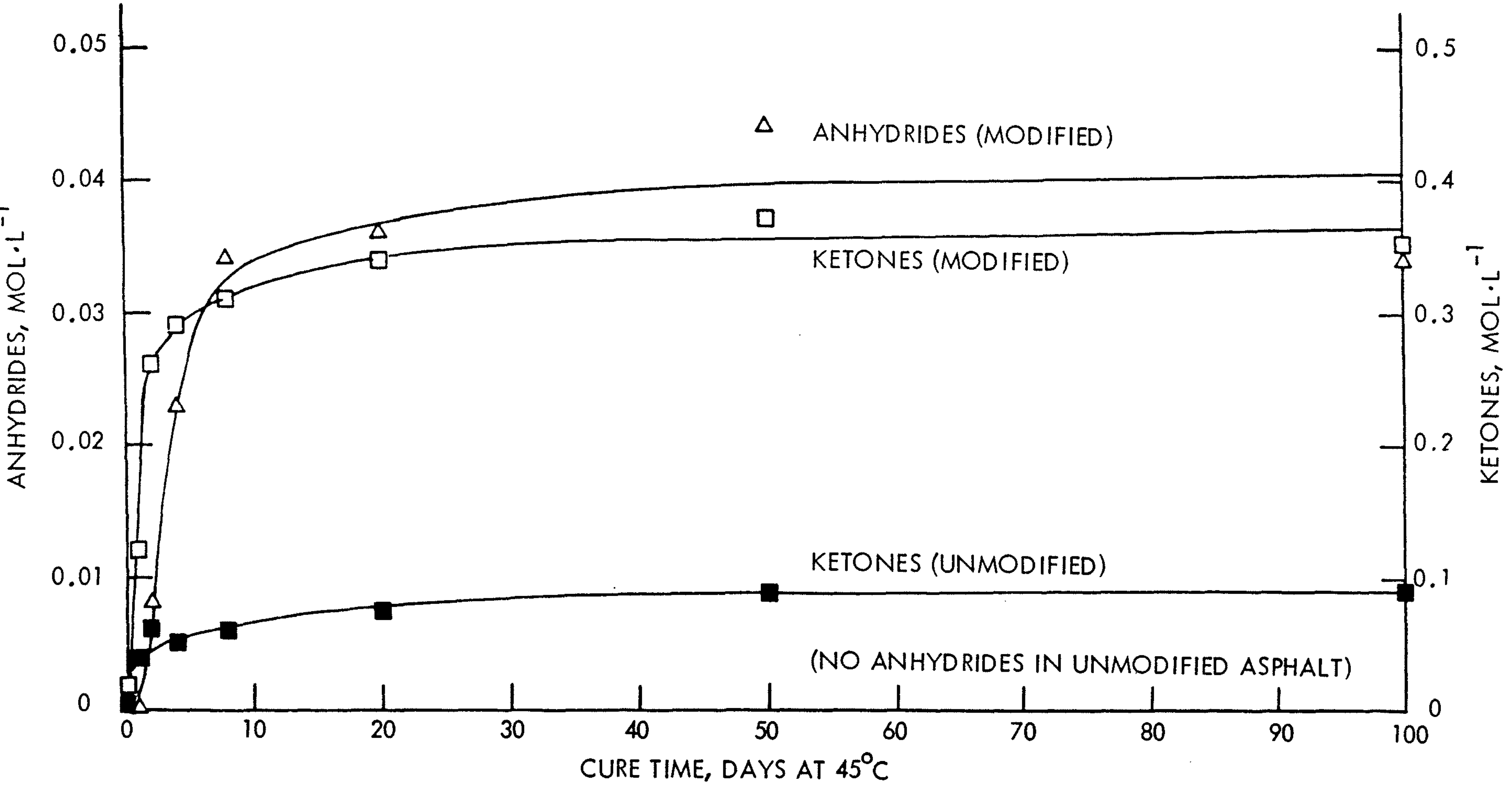


Figure 8. Ketone and Anhydride Formation During Cure of Manganese-Modified and Unmodified Wood River AC-5 Asphalt

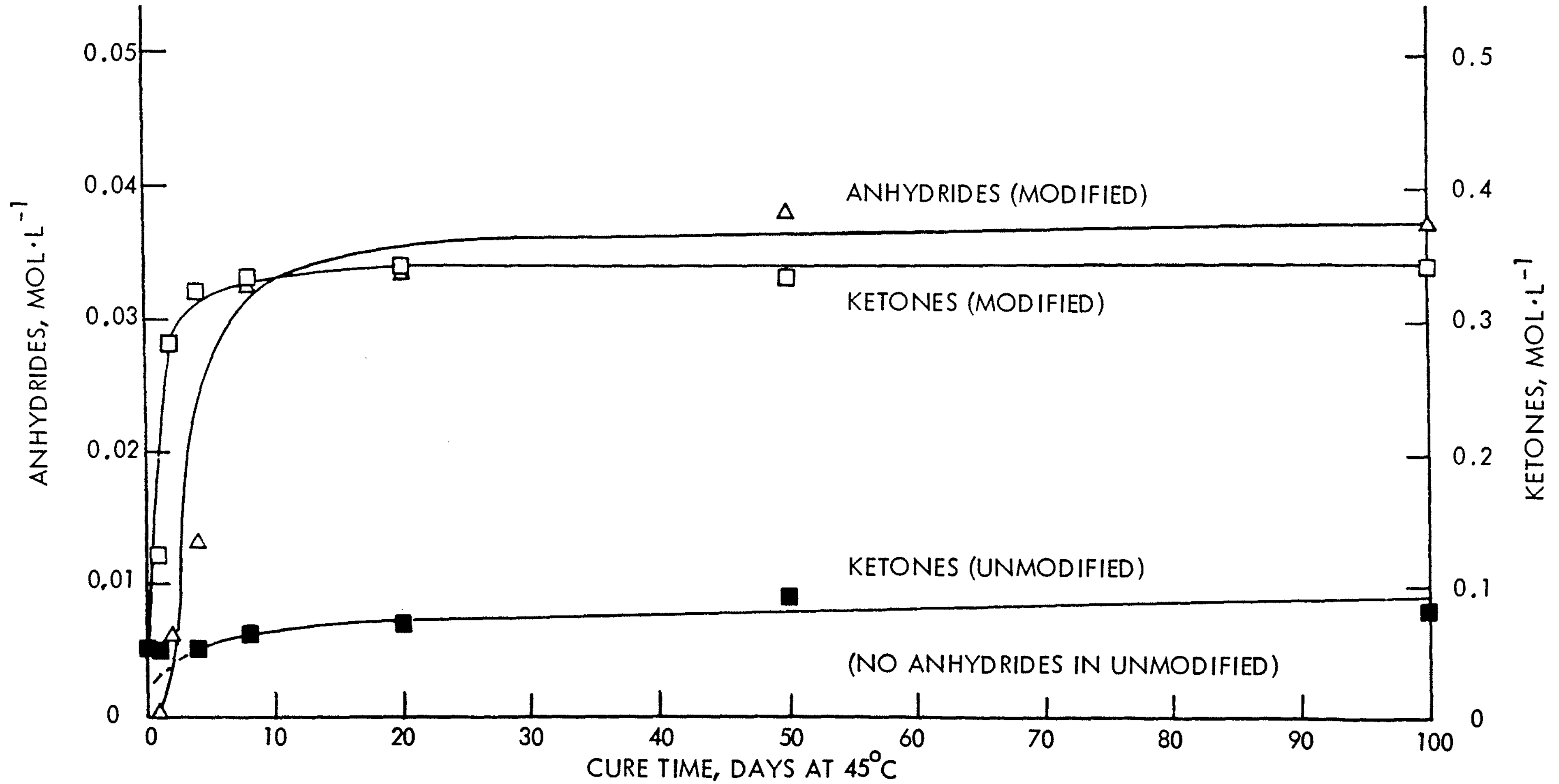


Figure 9. Ketone and Anhydride Formation During Cure of Manganese-Modified and Unmodified Wood River AC-20 Asphalt

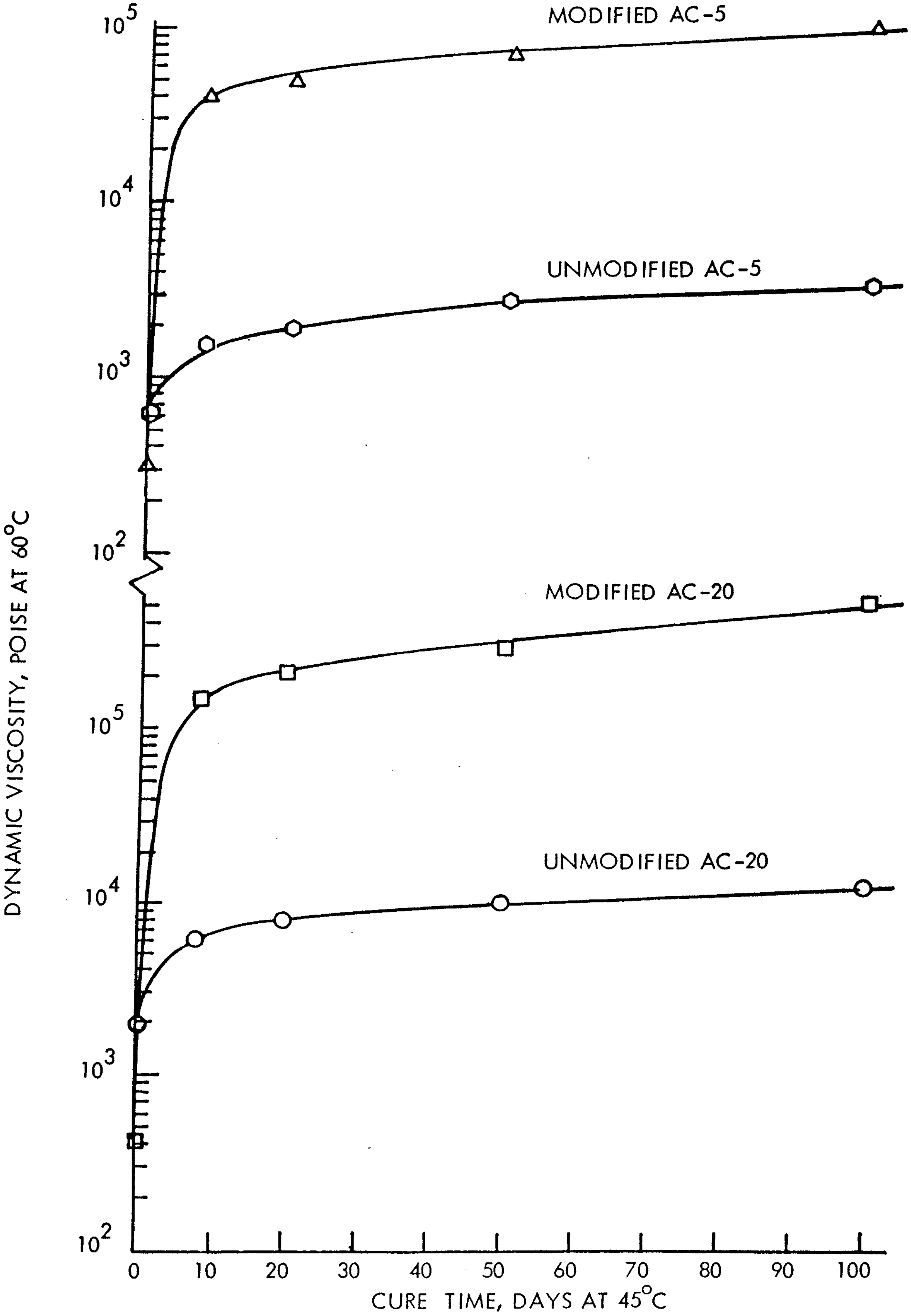


Figure 10. Change in Viscosity During Cure of Manganese-Modified and Unmodified Wood River AC-5 and AC-20 Asphalts

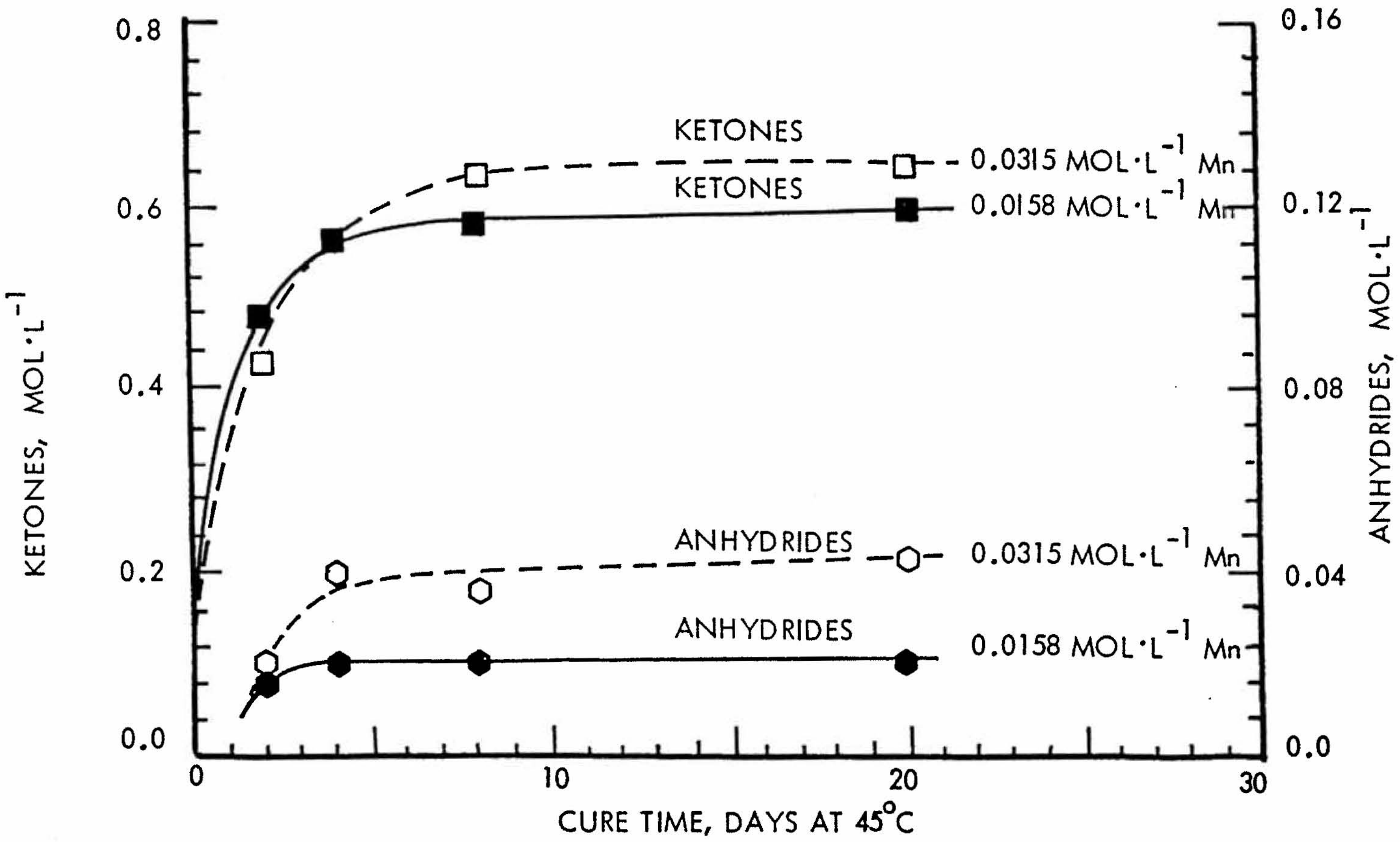


Figure 11. Effect of Modifier Concentration on Ketones and Anhydrides Formed in Asphalt B-3037 (AC-5) Using an Early Modifier Formulation

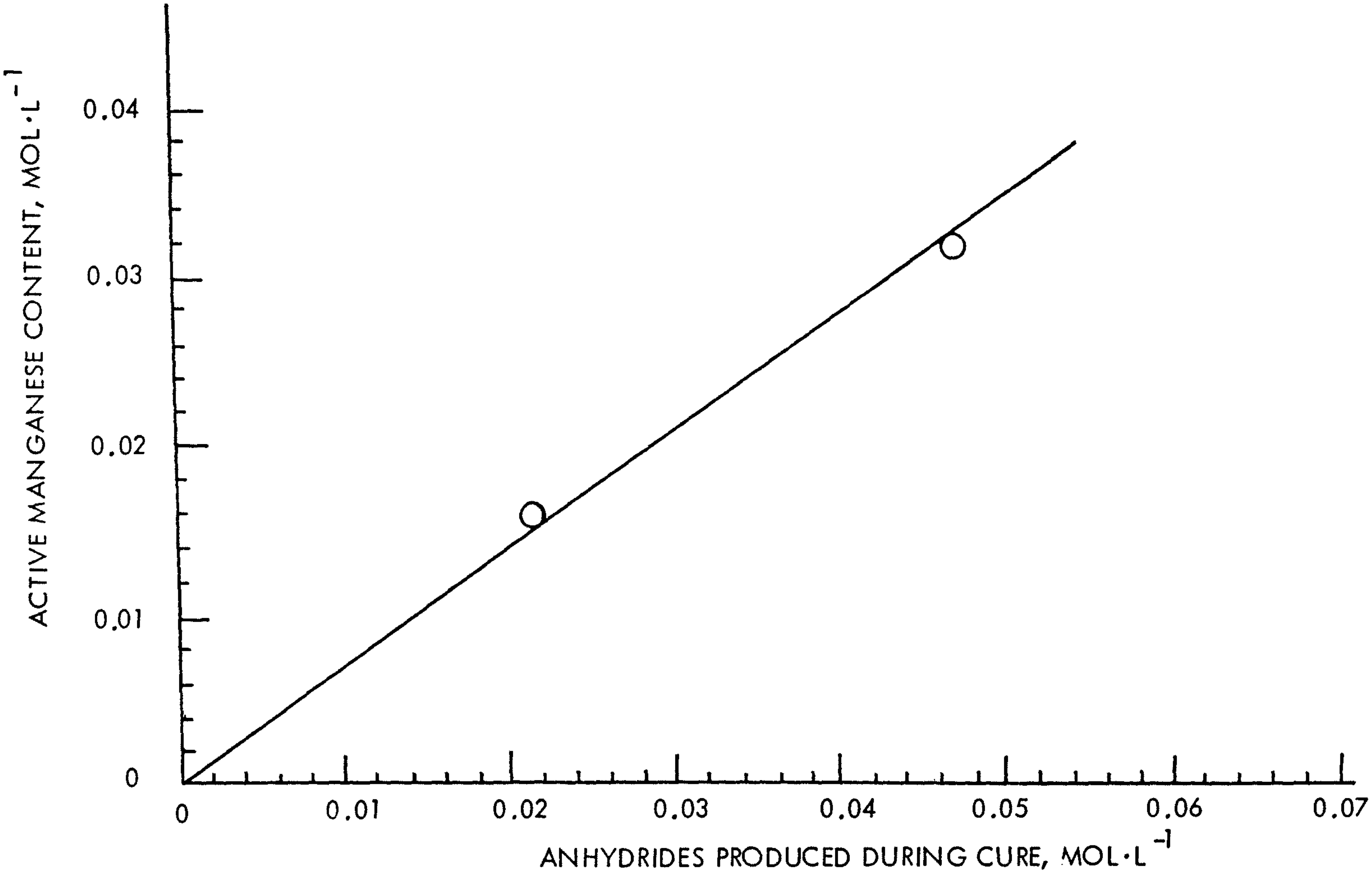


Figure 12. Relationship Between Manganese Content and Anhydrides Formed During Cure Using an Early Modifier Formulation

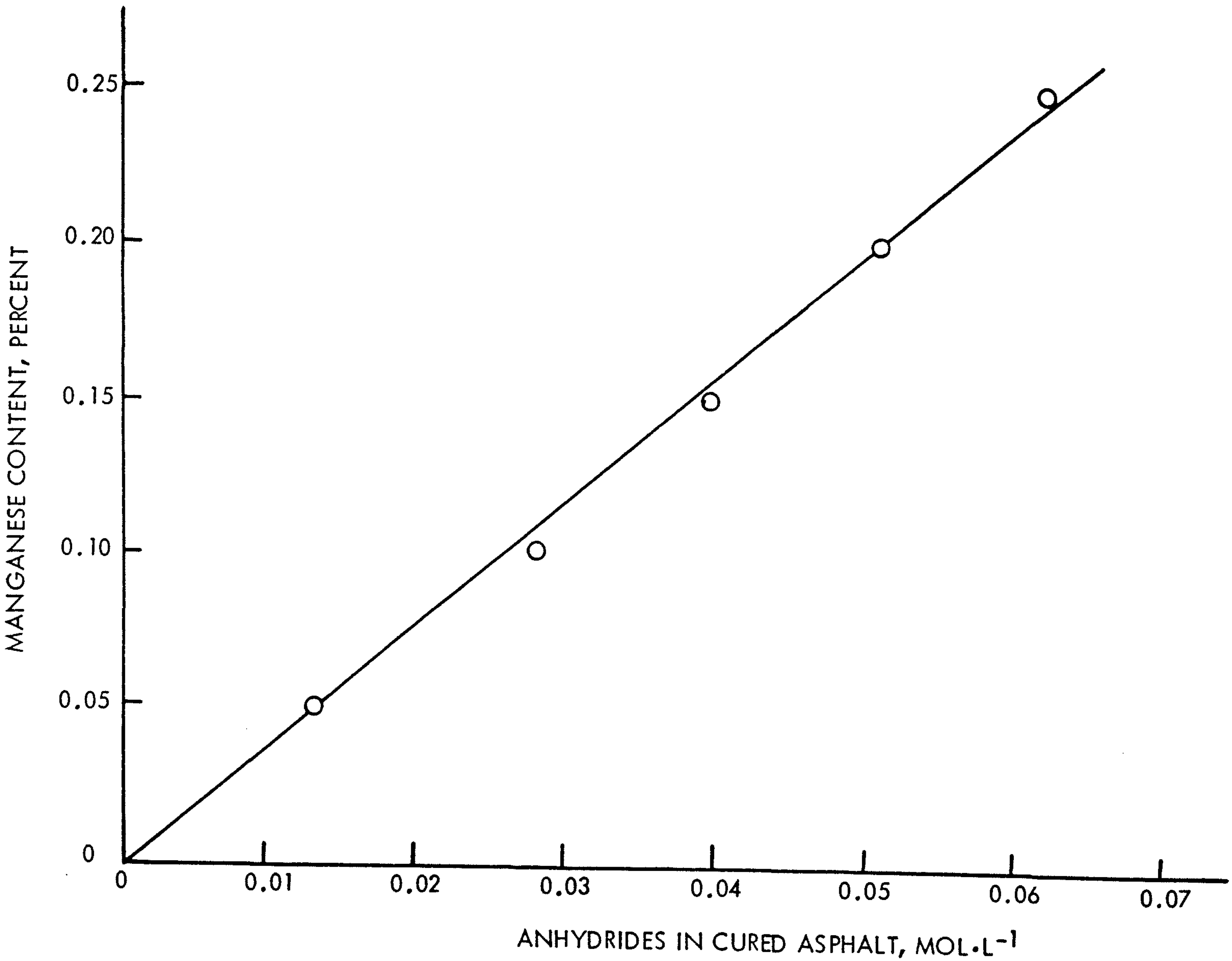


Figure 13. Relationship Between Manganese Content and Anhydrides Formed During Cure Using Current Modifier Formulation in Cosden AC-5 Asphalt

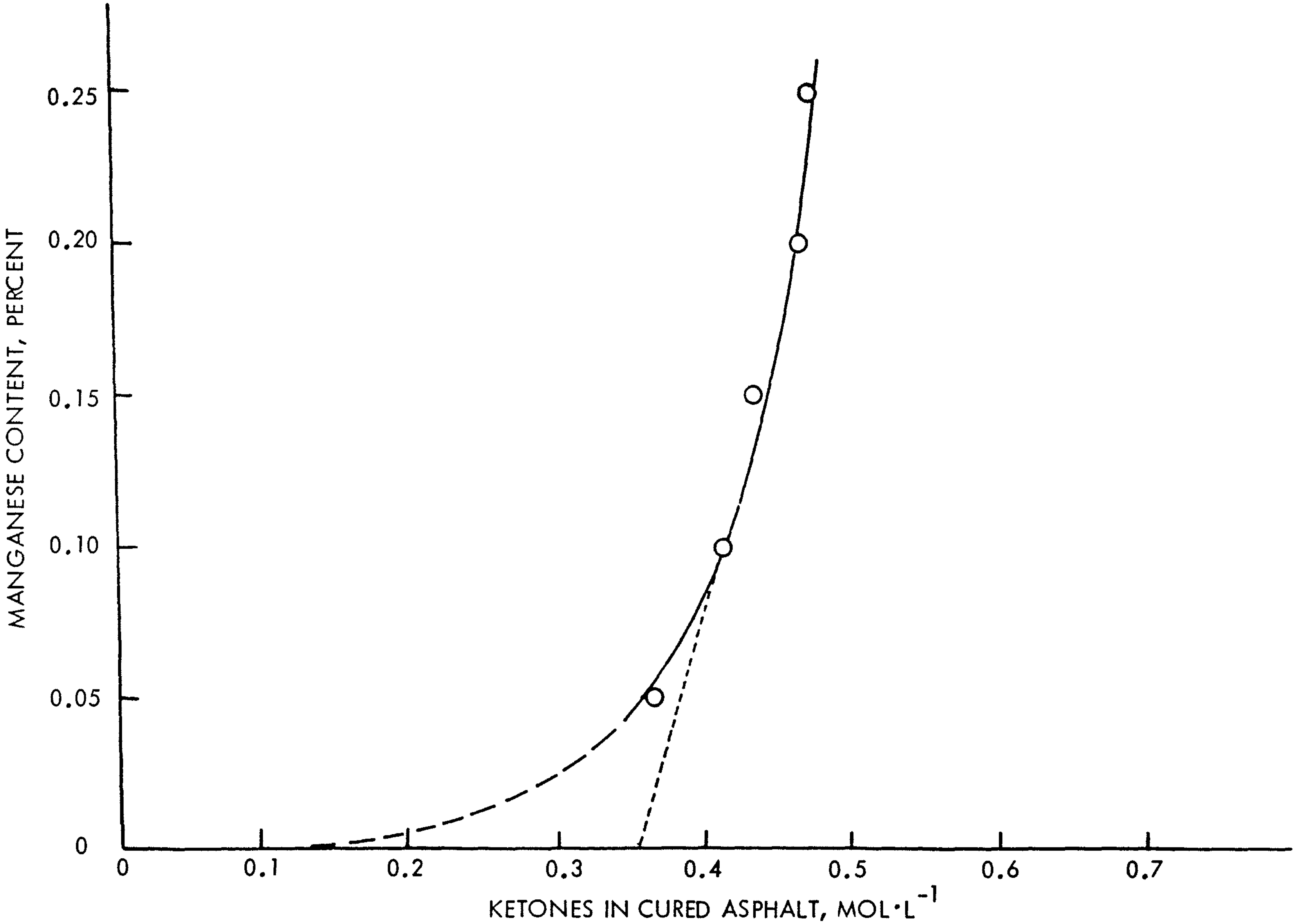


Figure 14. Relationship Between Manganese Content and Ketones Formed During Cure Using Current Modifier Formulation in Cosden AC-5 Asphalt

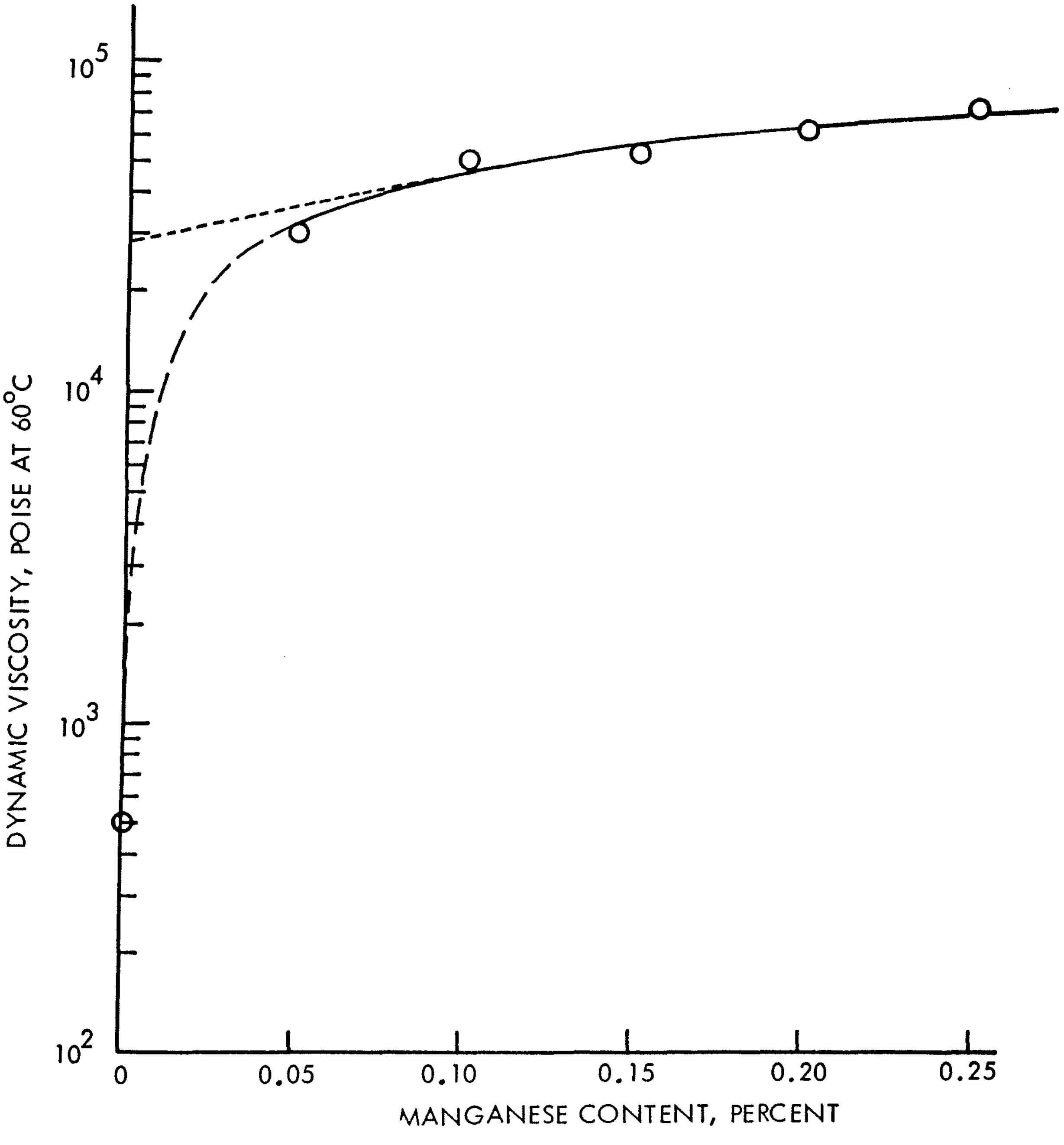
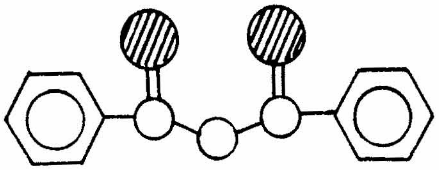
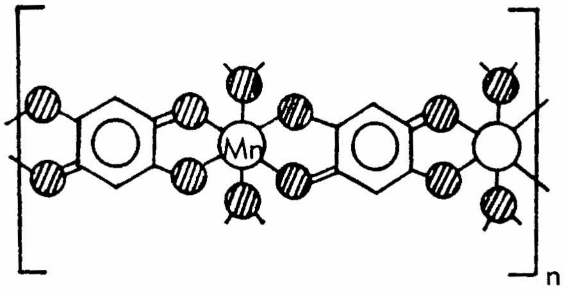


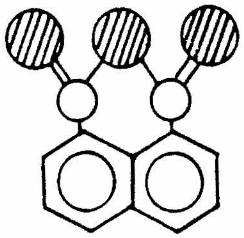
Figure 15. Relationship Between Manganese Content and Dynamic Viscosity of Cured Cosden AC-5 Asphalt Using Current Modifier Formulation



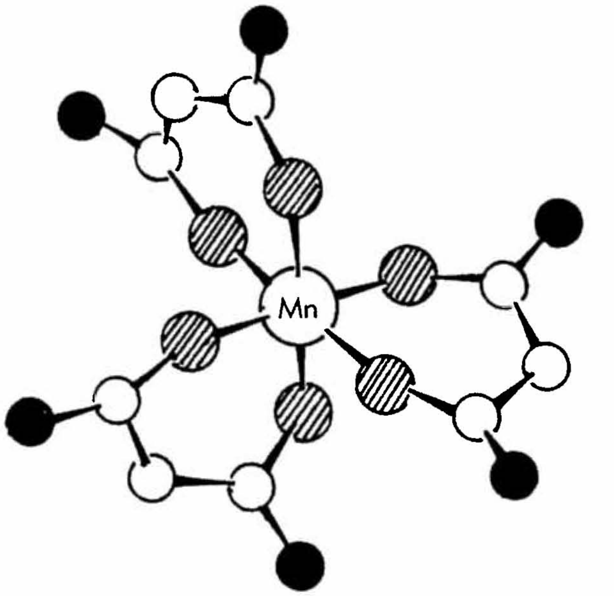
DIPHENYLMETHANE



1,5-p-BENZOQUINONE-MANGANESE COMPLEX



1,8-NAPHTHALIC ANHYDRIDE



ACETONYLACETONE-MANGANESE COMPLEX

Figure 16. Molecular Structures Associated with Manganese Complex Formation

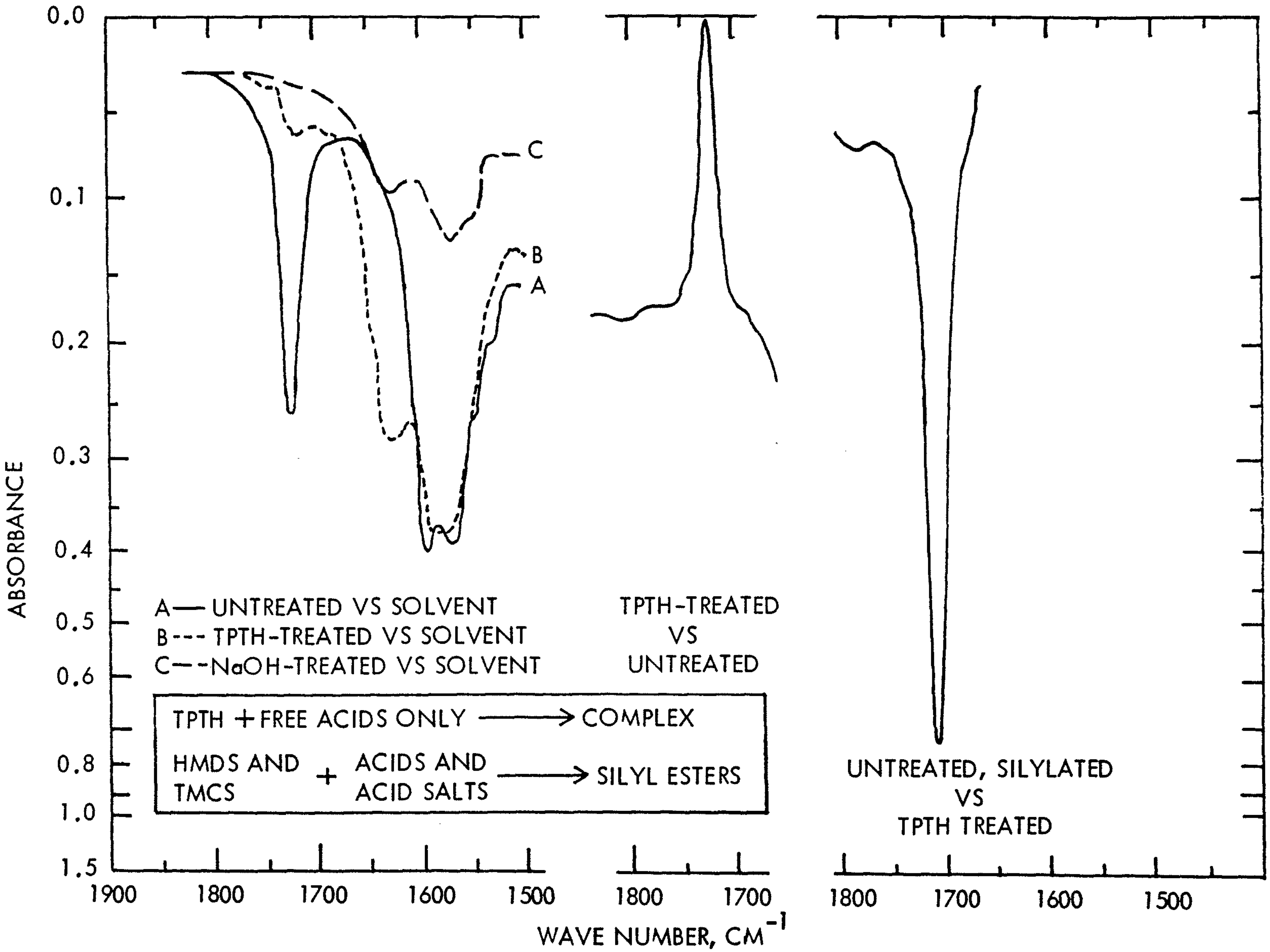


Figure 17. Example of Spectra Used in the Functional Group Analysis of the Manganese Modifier

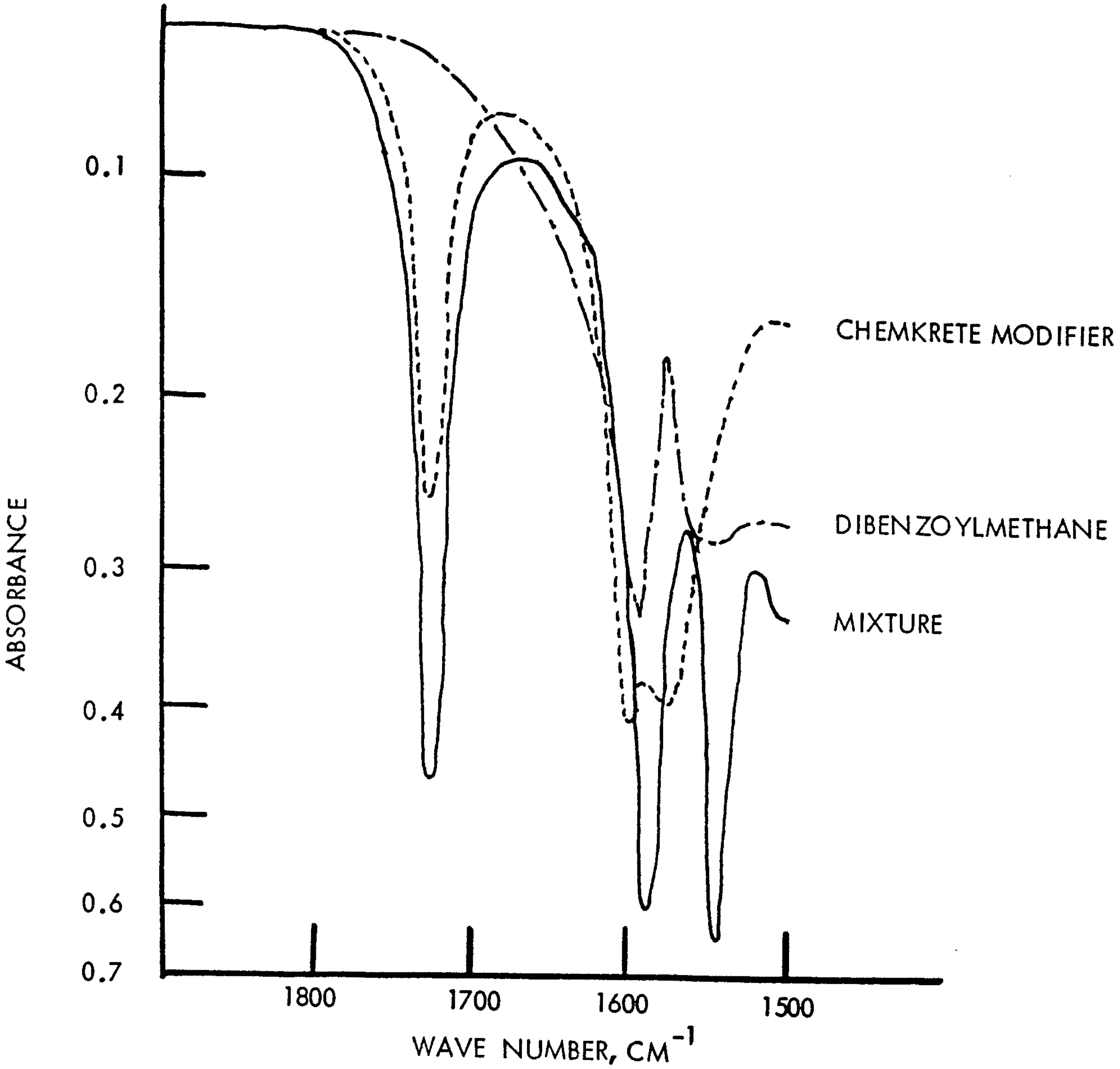


Figure 18. Infrared Spectra of the Manganese Modifier and its Coordinate Complex with Dibenzoylmethane

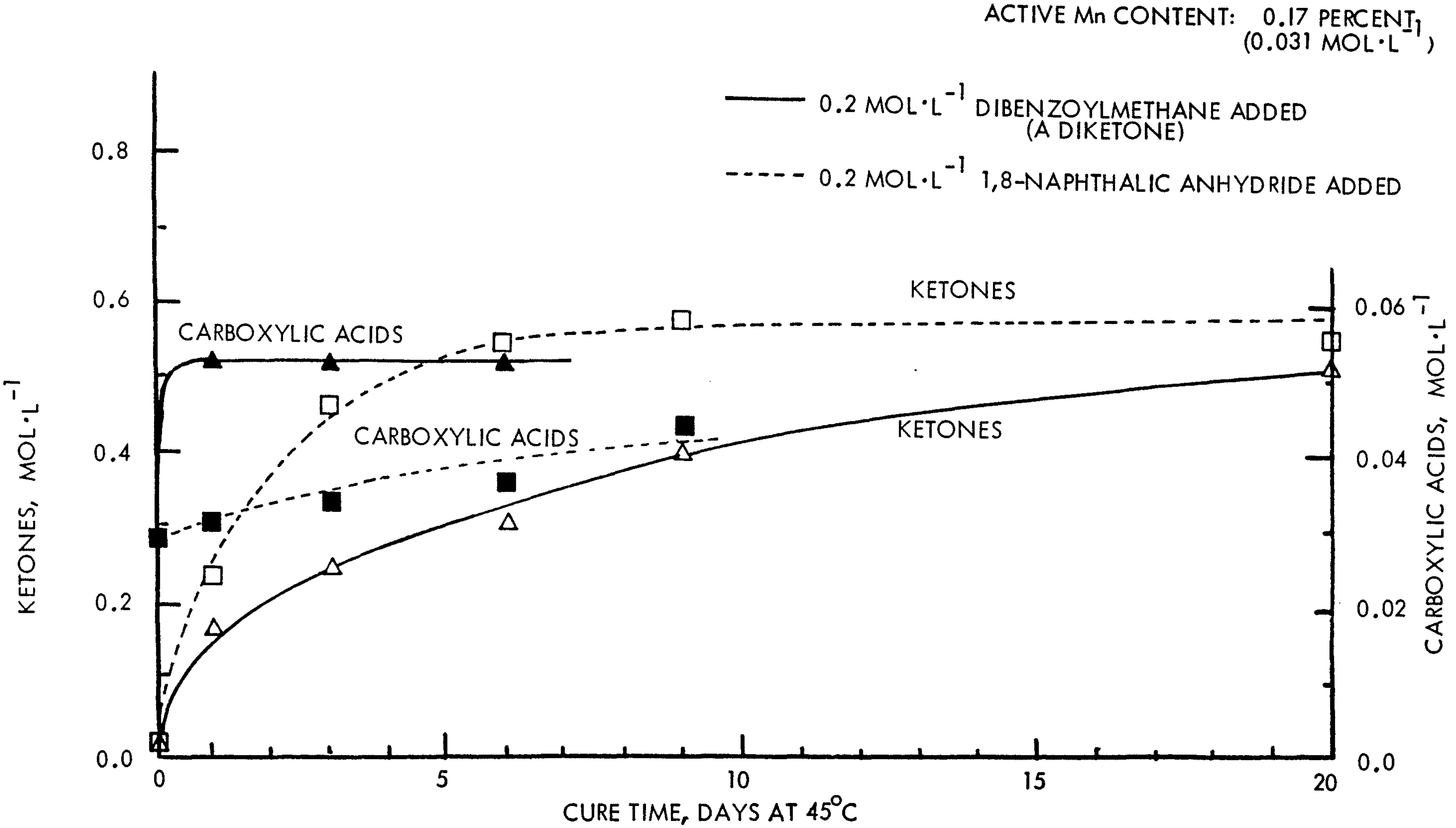


Figure 19. Curing Rate Data for Manganese-Modified AC-5 Asphalt B-3037 Spiked with Dibenzoylmethane and 1,8-Napthalic Anhydride

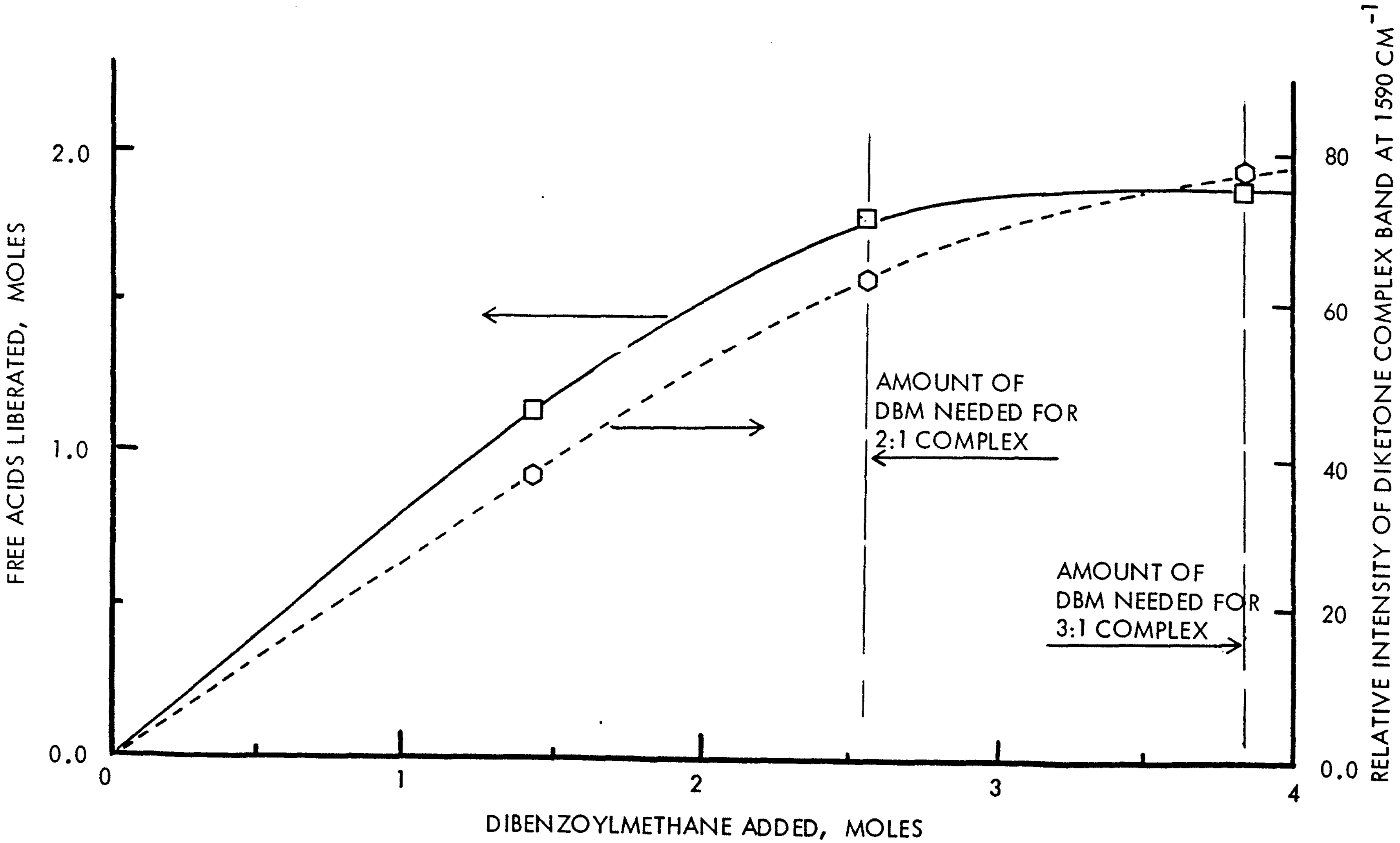


Figure 20. Free Acids Liberated and Diketone Coordinate Complex Formed by Reaction of Type 150.40 Manganese Modifier with Benzoylmethane

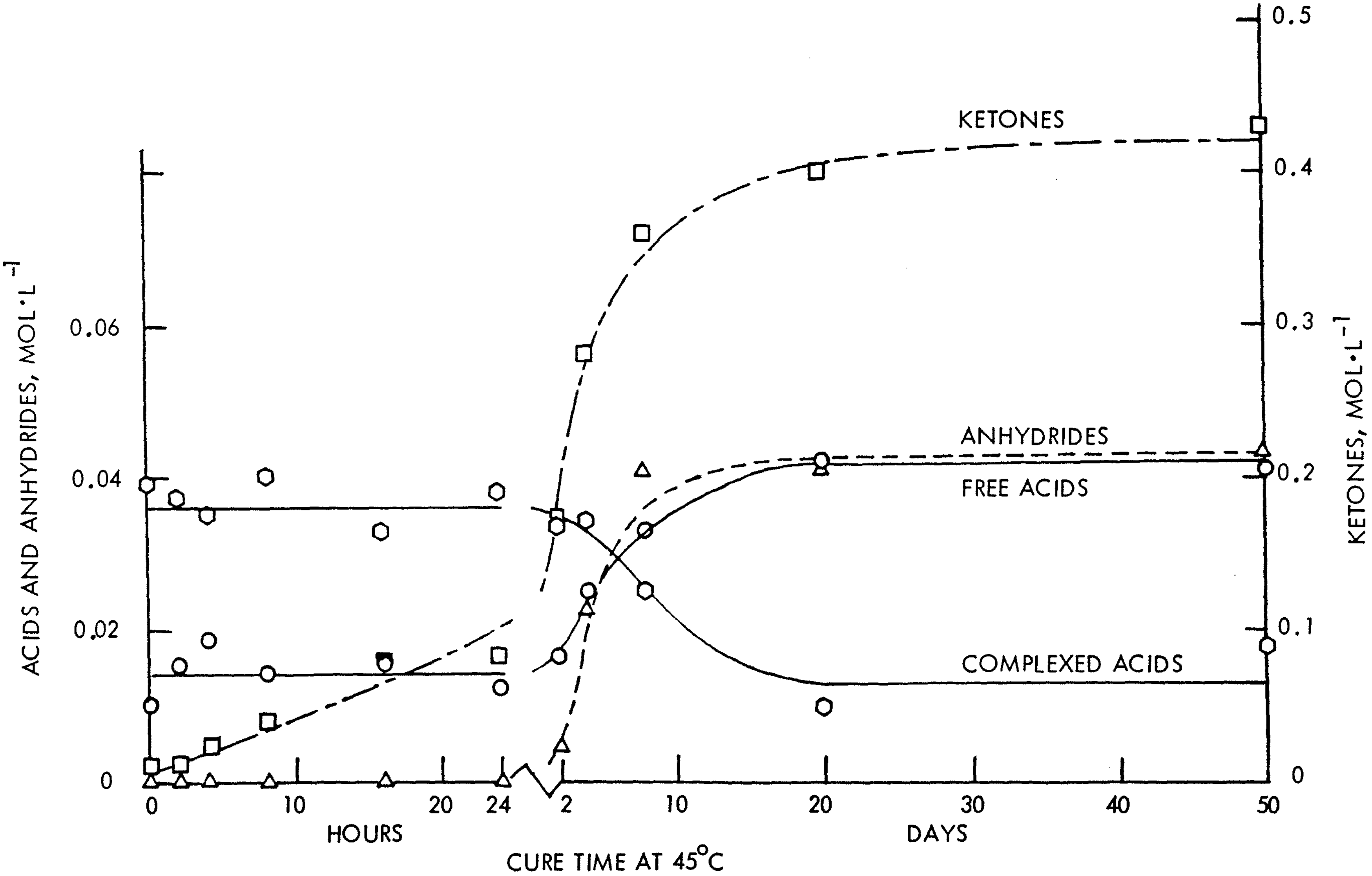


Figure 21. Changes in Chemical Functionality During Cure of Manganese-Modified Cosden AC-5 Asphalt