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ELECTRON PARAMAGNETIC RESONANCE ON ASPHALTIC MATERIALS

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Asphalts have been used as paving materials for many years and a great deal of research has been conducted in the physical properties needed for good performance. In the past, some chemical research has been performed on these materials as well. Questions have remained as to what chemical properties are important in the design of a long-lasting pavement structure. This study has used a spectroscopic technique to investigate the aging and catalytic properties of asphalts. Electron Paramagnetic Resonance (EPR) was used to identify the role of free-radical species in these processes. Two paramagnetic categories were identified: organic free radicals and vanadium transition metal ions. Free radical and transition metals are highly reactive, and may play important roles in the oxidation process that contributes to aging. The results of this study indicate that there may be a relationship between the concentrations of the free radical species to the aging index and to the changes in the specific clay-gel fractions. / Keywe & Co. /				
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PREFACE

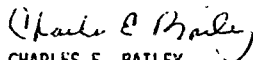
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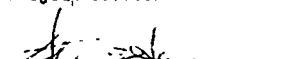
This report summarizes the work performed from October 1984 through September 1985. Mr Charles E. Bailey was the AFESC/RDCP project officer.

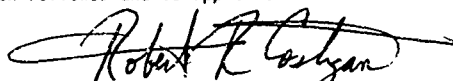
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This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Services (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.


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SECTION I INTRODUCTION

OBJECTIVE

The specific objective of this subtask was to perform a study utilizing Electron Paramagnetic Resonance (EPR) to establish baseline data on aging, oxidation, and inorganic catalytic processes for a variety of virgin asphalts, modifiers, blends, aged asphalts, and mixtures.

BACKGROUND

For many years, much research has been conducted to try to identify some performance criteria of asphalts used as paving materials. Most of this research has focused on the physical and rheological properties of bitumens as well as mixture properties that constitute a long-lasting pavement. However, some fundamental questions remain unanswered. The physical and rheological properties found in asphalts are a manifestation of the chemical processes taking place on a molecular level. Only in the last 10 or 15 years has an emphasis been placed on the chemistry of these materials. While the pavement engineer must ultimately deal with physical properties, fundamental understanding of the chemical properties is imperative to better utilize materials and improve performance.

One of the problems is the aging of pavements and ultimately, the breakdown of the pavement macrostructure. This results either in very expensive temporary repairs, or complete reconstruction of the old pavement. Engineers need to design and construct pavements that have a long design life and require a minimal amount of repair. To do this, engineers must know as much about the materials used in the asphalt concrete as possible. One mechanism in the asphalt aging process is the oxidation of certain chemical fractions of the asphalt binder. This oxidation process is generally thought to produce asphaltenes as an end product. According to this reasoning, the buildup of high concentrations of asphaltenes then causes the hardening of the binder and, finally, the breaking of the asphalt-aggregate bond, which in turn results in the breakup of the pavement structure.

magnetic behavior of the electron is modified by the magnetic fields in its surroundings. This deviation from the standard behavior can be used to investigate the structure of the material in question.

Asphalt is a very complex mixture of many different organic and inorganic molecules. Chemical information is difficult to obtain from asphalt, due to its complex makeup and to the problems encountered in separation of different species. Since EPR is peculiar to molecules having unpaired electrons, and since few asphaltic species have unpaired electrons, EPR is especially appropriate for use in the study of asphalt. An additional advantage to use of EPR is its sensitivity to very low concentrations of these paramagnetic species. Molecular species that contain unpaired electrons are usually very reactive (because electrons favor covalence); and these unpaired species are probably involved significantly in oxidation and aging. This EPR spectroscopic technique has been used to investigate the processes that may be contributing to the aging and oxidation mechanisms.

SCOPE/APPROACH

To understand the aging and oxidation of asphalts from a more fundamental level and to determine the influences of paramagnetic molecular species on these processes, an in-depth investigation into the chemistry of asphalts is needed. This research effort was aimed at utilizing EPR to study the oxidation, aging, and inorganic catalytic processes occurring in asphaltic materials. A comprehensive literature review of previous and current research in the area of EPR relating to petroleum products was conducted to establish the current state of the art. Studies then began on a variety of asphalts, modifiers, blends, and mixtures, using EPR. The purpose of these studies was to arrive at a molecular definition of ongoing oxidation, aging, and catalytic processes, to correlate these definitions with physical and chemical data, and to relate these properties to the results in this study.

This research was completed in two phases. Phase I efforts were accomplished under contract F29601-81-C-0013, Subtask Statement 5.11, and included the literature review, spectra gathered from virgin and aged asphalts, solvent

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effects, and a limited number of spectra on various clay-gel fractions. An interim report was submitted as a summary of Phase I efforts.

Phase II included EPR studies on additional virgin asphalts, mixtures, unaged and aged asphalts, materials with and without fines, additional clay-gel fractions, and a limited number of aggregates. The concentrations of the EPR-active species were determined before and after aging. These species included the organic free radicals, and the metallic paramagnetic species. Their concentrations were correlated with other chemical data, such as clay-gel percentages, and with physical parameters. Concentration changes upon aging were also examined and correlated with physical changes. The paramagnetic metallic species were examined closely to determine possible catalytic activity that might promote oxidation and aging.

This report documents the literature review, testing and materials, test data, correlations, discussion, recommendations, and postulations from Phases I and II.

SECTION II

LITERATURE REVIEW

Past studies have investigated paramagnetic species in crude oils, asphaltenes derived from crude oils, and coal-derived asphaltenes. Much of that work has centered on the presence and form of paramagnetic metallic species. In 1924, Nellenstyn (Reference 1) proposed that the metals may be present as inorganic crystals and form a nucleus of a colloidal system. Shirey (Reference 2) proposed that these metal species may be in the form of organo-metallo complexes. Dunning and co-workers (Reference 3) utilized EPR to categorize the paramagnetic species in crude oils. These categories included: volatile and vanadyl (i.e., prophyrin) complexes; volatile and nonvanadyl; nonvolatile and vanadyl; and nonvolatile and nonvanadyl. Based on more extensive studies using EPR, Saraceno and co-workers (Reference 4) and Roberts and co-workers (Reference 5) indicated that almost all of the vanadium in crude oils exists as vanadyl complexes similar to etioporphyrin I complex.

Retcofsky and co-workers (Reference 6) conducted a study of coal and coal-derived asphaltenes using EPR. They found that the concentrations of unpaired electrons increase with increasing coal rank, up to a carbon content of approximately 94 percent, after which the spin concentrations decrease rapidly. They postulated that the initial increase in spin concentration is due to the formation of organic free radicals during vitrification. The free electrons are probably delocalized over aromatic rings and stabilized by resonance. However, when the carbon content reaches 94 percent or higher, the conductivity of the samples is increased, causing the dramatic decrease in the spin concentrations.

Retcofsky and co-workers (Reference 7) studied the nature of the free radicals in coals, pyrolyzed coals, and solvent-refined coals, to explain the role of these radicals in the coal liquefaction process. They correlated the EPR g-values with oxygen content and sulfur content, and found a linear correlation. This indicates that oxygen and sulfur atoms may play an important role in the structure of free radicals.

In a study by Boucher and co-workers (Reference 8), the spectral properties of oxovanadium(IV) complexes have been investigated using EPR. They looked extensively at several parameters such as A values and g values for both the parallel and perpendicular components. They used these values in determining the environment of the vanadium, the solvent influences, the geometry of the oxovanadium complex, and the hydrogen-bonding effects. The data were obtained on model compounds, and not complex systems such as petroleum or coal; however, this study has established some baseline data that can be used to determine the environment of the vanadium in asphalts. Another study by the same researchers (Reference 9) used visible spectroscopy and EPR to investigate some oxovanadium(IV) complexes and the influences of solvents on the spectra, and to compare the β -ketimines to β -diketones and porphyrin complexes.

Yen and co-workers (Reference 10) investigated free radicals in petroleum asphaltenes using EPR. They reported that the g-values were close to those found in free radicals of aromatic systems. They calculated the spin concentrations and found that they correlated with the hydrogen/carbon ratio, oxidation rate, aromaticity, and color intensity. They also postulated that the free radicals are associated with nonlocalized systems in the aromatic centers. Yen and co-workers also proposed structures which may be sites of free electrons in petroleum asphaltenes. Their structures are based on gaps or holes that result when heteroatoms such as oxygen, nitrogen, and sulfur cannot form as many bonds as carbon. These sites offer sites for stable, free electrons. Gaps in aromatic clusters are also suggested as possible sites for unpaired electrons. Tynan and Yen (Reference 11) revealed two different types of vanadium occurring naturally in petroleum. They studied a Venezuela asphaltene in solutions and found one type of vanadium to be "bound" and the other "free." With increasing temperature or dilution, the bound type seems to be gradually shifted toward the free type. They suggested that the vanadium chelates may be trapped between sheets of aromatic molecules, and for the release of these complexes to occur, a distinct amount of energy must be introduced into the system.

Characterization of vanadium(IV)-sulfur species in petroleum by using EPR was performed by Dickson and co-workers (Reference 12). They attempted to identify the environments that the vanadium may be located. By examining the g-values of the polar and nonpolar portions of the petroleum residuals, they suggested that the polar portion contains vanadium species coordinated with a ligand that includes nitrogen and oxygen, while the nonpolar fraction contains ligands having four sulfur atoms in the coordinating positions.

Other researchers (References 13, 14, 15, and 16) have used EPR as a probe to study the temperature dependence of vanadyl complexes, impurities, molecular phases, and electron-spin echoes and saturation in coals. Sebor, Kubelka, and Weisser (Reference 17) used a variety of techniques to separate and characterize vanadyl porphyrins from Romashkino petroleum. They included precipitation with n-pentane, separation by column chromatography, ultraviolet and visible spectroscopy, mass spectroscopy, and atomic absorption spectroscopy. They also identified several types of porphyrins present in the asphalt fraction of the petroleum.

However, Branthaver and co-workers (References 18 and 19) have performed significant work in the area of metalloporphyrins and their effect on asphalt oxidation. In the first study, two different asphalts were artificially aged and oxidized for 24 hours, using several different metal chelates as additives. The two asphalts used in this study contained low (less than 20 ppm) concentrations of vanadium and nickel. Four metal chelate additives were used. Infrared spectroscopy was used as the probe to determine whether the additives promoted oxidation by calculating the concentrations (before and after oxidation) of the several functional groups (ketone, acid, and anhydride functions). Their results show that vanadyl porphyrins can promote asphalt oxidation. This oxidation is not directly related to the total amount of vanadyl porphyrin, but is influenced by other factors. The substituents located on the vanadyl molecule may influence the effectiveness of the catalyst. The second study (which involved four asphalts mixed with fractions rich in vanadyl chelates prepared from two crude oils) was conducted to observe the same phenomenon as the first. An additional observation was that a direct correlation of vanadyl porphyrin concentration with asphalt oxidation exists only if asphalts are mixed with varying amounts of the same fraction

derived from the same crude. The probable causes are differing oxidation susceptibilities of various asphalts, molecular associations, and the relative catalytic activities of metalloporphyrins and other metal chelates.

A recent study investigated the oxidation of butane, using a vanadium catalyst (Reference 20). Butane is a saturate-like molecule; and this study suggests that a vanadium catalyst promotes the otherwise very difficult oxidation process. This may be significant in analyzing why some asphalts have small changes in the saturate fraction of the asphalt after aging, while others have no noticeable change.

Except for the last few studies listed in the literature review, most of the work has concentrated on coal and petroleum. Even though these investigations were conducted on different materials, they are similar enough to asphalts to offer much information that can be related to the materials studied in this effort. The last three studies listed above have provided an immense amount of information needed for this effort.

SECTION III

MATERIALS AND TESTING

MATERIALS

The materials used in this research effort consisted of a variety of neat asphalts, modified extracted binders from freshly prepared mixtures, rolling thin film oven (RTFO)-aged binders, oven-aged extracted binders, field-aged extracted binders, and aggregates. Many of the materials were the same as those used in previous and current studies conducted at the New Mexico Engineering Research Institute (NMERI). The neat asphalts used included viscosity-graded materials of 500, 2000, 3000, and 4000 poises, as well as a penetration-graded asphalt of 85/100. The modifiers and field-aged extracted binders tested were selected from materials used in another research effort conducted by NMERI for the U.S. Air Force. The oven-aged extracted binders were from Marshall specimens prepared specifically for this effort from fresh asphalt binder and aggregates. Table 1 lists the materials tested.

TESTING

Testing consisted principally of obtaining EPR spectra of the materials; from this information, the spin concentrations of the organic free radicals and vanadium(IV) were calculated. Many of the materials listed in Table 1 were involved in Phase I, and were used for scoping the materials to use in Phase II for more intensified analysis. Several of the original materials were selected for spin concentration measurements. Of those selected, three asphalts were chosen for use in preparation of the Marshall samples as well as the aging process. These asphalts were Huntway AC-40, Husky AC-5, and Chevron AC-20. Materials were analyzed for total vanadium concentrations using atomic absorption spectroscopy. Neat asphalts and binders extracted from mixtures were analyzed for viscosity and clay-gel composition. Table 2 lists the viscosity data and aging indices for Huntway, Husky, and Chevron materials used in this study. Two viscosity values (unaged, and aged 154 days; both obtained at 140°F) for the extracted binders are given.

TABLE 1. MATERIALS TESTED.

1. Chevron AC-20	Neat, clay-gel fractions, RTFO, with and without solvent, clay-gel fractions of RTFO, 154-day-aged binder.
2. Huntway AC-40	Neat, clay-gel fractions, RTFO, with and without solvent, clay-gel fractions of RTFO, 154-day-aged binder.
3. Husky AC-5	Neat, clay-gel fractions, RTFO, with and without solvent, clay-gel fraction of RTFO, 154-day-aged binder.
4. Chevron AC-10	Neat, clay-gel fractions, RTFO, clay-gel fractions of RTFO.
5. Chevron 85/100	Neat, with and without solvent.
6. Navajo 85/100	Neat, clay-gel fraction of neat and RTFO.
7. Cosdon 85/100	Neat, clay-gel fractions of neat and RTFO.
8. Southern Union	Neat, clay-gel fractions of neat and RTFO.
9. Recycling agents	Shell RA500, Cyclogen L, Dutrex 739, Chevron HMA5.
10. Georgia	Wet and dry, lime-treated sample.
11. Mississippi	Wet and dry, Pavabond LP-treated sample.
12. Blends	MBD-51, MBD-52, MBD-53, MBD-8A1, MBD-8A2, MBD-8A3, plus RTFO of these blends.

TABLE 2. VISCOSITY OF EXTRACTED BINDERS, AND AGING INDEX,
FOR TESTED MATERIALS.

Asphalt product	Viscosity, Poises, at 140 °F		Aging index
	Unaged	Aged	
Huntway AC-40	4,033	290,343	72.70
Husky AC-5	610	49,691	81.46
Chevron AC-20	1,883	43,309	23.00

Physical Characterization

Viscosity of the materials was obtained, using ASTM D-2171 at 140°F. Extraction of the binders from mixes was accomplished, using ASTM 2172 with one modification. A Buchi rotary evaporator was used to recover the binder from the solvent. This method decreases the time element, and removes the solvent more effectively. The mixtures were prepared, using the standard Marshall method of preparation. These Marshall mixtures were oven-aged at 140°F for 154 days, and were extracted after the aging period for further testing.

Chemical Characterization

Three methods of chemical characterization were used in this study: total vanadium analysis by atomic absorption, compositional analysis by the modified clay-gel, and spin concentration measurements by EPR spectroscopy. Each of these methods is discussed in detail in the following subsections.

Total vanadium analysis was obtained using atomic absorption spectroscopy. To obtain a sample that can be analyzed, the asphalt sample is ashed, and the ash material placed in a flame. Since the vanadium is inorganic in nature, the ashing process does not destroy any of the vanadium but does reduce the organic components to CO_2 and H_2O . The absorption radiation corresponds to specific elements in the test material. The radiation corresponds exactly to the energy required for a test element transition from the ground state to an upper, excited level. The radiation absorption depends on the ground-state population, which is proportional to the solution concentration sprayed into the flame. Absorption is measured by the difference in transmitted signal in the presence and absence of the test element. The total vanadium concentration is then reported. This particular technique cannot distinguish between the total vanadium and the vanadium(IV) concentration. The results from this analysis are reported in parts per million (ppm) by weight.

Compositional analyses were performed, using the Clay-gel Compositional Analysis Method (formerly ASTM D-2007-75). However, modifications have been made, to encompass a variety of asphalts, modifiers, blends, and extracted binders (Reference 21). Appendix A outlines and explains the modifications incorporated into the method. Four fractions are obtained from the separation process; asphaltenes, polars, aromatics, and saturates. These are listed in descending order of polarity. Using the modified method, a sample of asphalt is dissolved in n-pentane and the asphaltenes are filtered, using a Buchner funnel. The maltenes are then charged into two columns in series, one packed with attapulgus clay and the other with silica gel. Using n-pentane, the saturates are eluted from the columns first. The two columns are then separated. The aromatics are stripped from the silica gel column using toluene and acetone, and the polars are stripped from the clay column. The solvents are evaporated and percentages of the fractions are calculated. This modified method has been used in other research efforts conducted at MMERI for the U.S. Air Force and has proved to be very informative in defining correlations between physical and chemical parameters. The modified method only separates the asphalt into generic fractions (or general classes) of many different kinds of molecules. The saturate fraction, for example, contains mostly aliphatic hydrocarbon-type molecules (which can be straight or branched chains). The aromatic fraction probably contains aromatic systems that contain one or two rings.

The principal emphasis in this research effort was to utilize EPR spectroscopy to define reactive species and catalytic action, and to determine how these relate to aging and oxidation. EPR is a spectroscopic technique in which radiation of microwave frequency induces transitions between magnetic energy levels of electrons with unpaired spins. These unpaired electron species are very reactive, and thus may contribute significantly to the oxidation and aging of asphaltic materials. One advantage of the EPR technique is that solid samples can be analyzed without using solvents, which break up the molecular structuring and alter the spectrum obtained. Using the selected procedure, an asphalt sample, contained in a 10-millimeter inner diameter quartz tube, is placed in the microwave cavity. A magnetic field and microwave field are applied, causing the electrons to align with the magnetic field and absorb energy, elevating them to a higher energy level. This absorption of microwave radiation is converted to a derivative curve, from

which identification of the unpaired electron species and the spin concentrations can be obtained. The two kinds of species usually found in the EPR spectrum of asphalts are organic free radicals and metal complexes. Each species gives distinct peaks and, when sweeping the magnetic field, is easily identified by its number of peaks and their location. Organic free radicals usually show a single peak, absorbing around 3400 gauss. The metal species produce multiple peaks, with a broader range of absorption energies. In the case of vanadium, the electron spin (7/2) results in an eight-line spectrum, calculated from the equation:

$$\text{number of peaks} = 2n + 1 \quad (1)$$

where n is the electron spin. For manganese, the spin (5/2) results in a six-line spectrum. Figures 1, 2, and 3 illustrate these spectra. Figure 1 shows the one-peak spectrum of an organic free-radical species. Figure 2 illustrates the spectrum of an organic free radical and the characteristic eight-line spectrum of vanadium(IV). Figure 3 is a manganese(II) EPR spectrum showing the six peaks found in this metal species. In the case of the metal complexes, only certain oxidation states have unpaired electrons which are EPR-active. In the case of vanadium, the +3 and +4 oxidation states are EPR-active; however, only the +4 species is strong enough to be observed by EPR. Manganese(II) is the EPR-active oxidation state for this species.

The curves or spectra obtained are digitized and the areas are calculated using a computer program. The areas are then used to calculate the spin concentrations of the respective species. The formula used for this calculation is listed in equation 2, below.

$$[x] = \frac{\text{Area}_x \cdot R_x \cdot (\text{scan}_x)^2 \cdot \text{gain}_{\text{std}} \cdot \text{mod}_{\text{std}} \cdot (g_{\text{std}})^2 [s(s+1)]_{\text{std}}}{\text{Area}_{\text{std}} \cdot R_{\text{std}} \cdot (\text{scan}_{\text{std}})^2 \cdot \text{gain}_x \cdot \text{mod}_x \cdot (g_x)^2 [s(s+1)]_x} \quad (2)$$

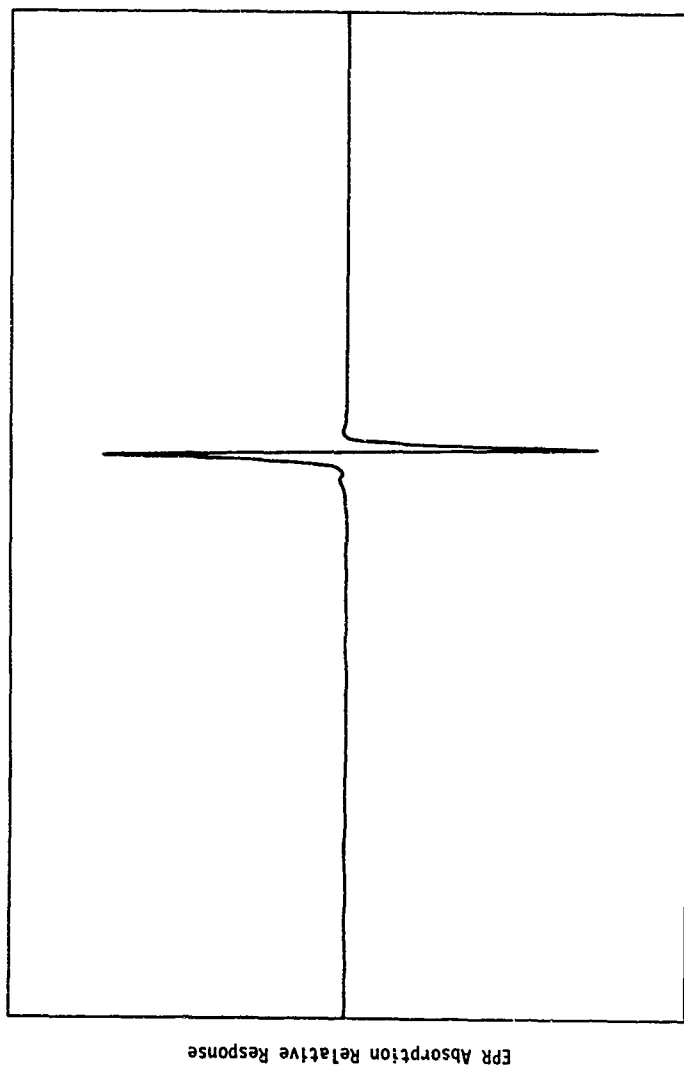
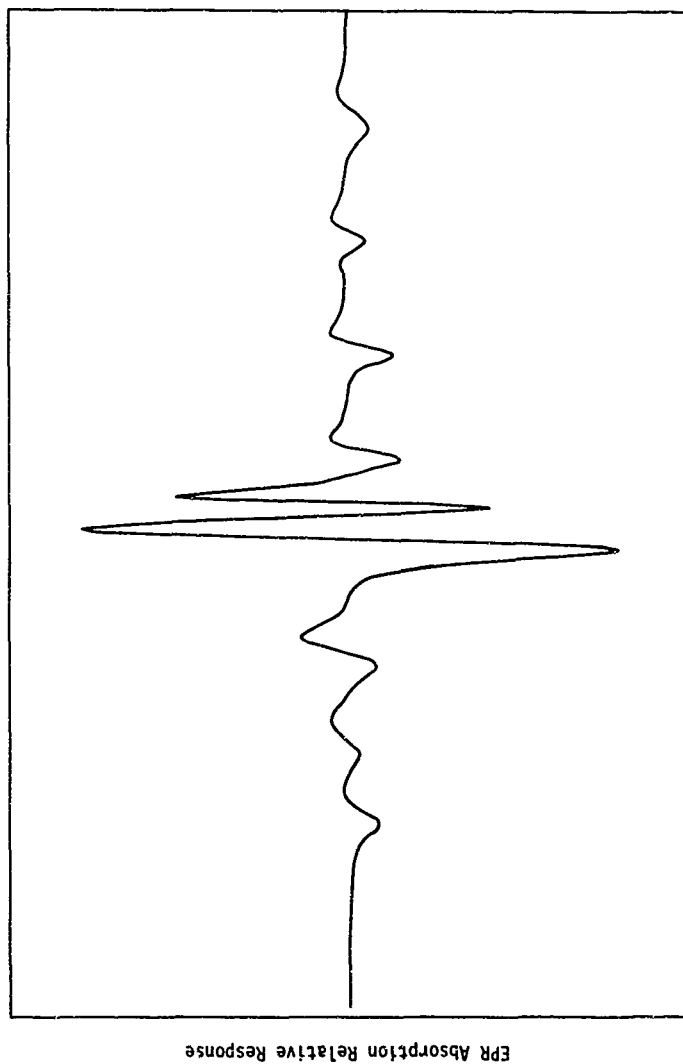


Figure 1. EPR Spectrum of Organic Free Radical Peak.



EPR Magnetic Scan Range, Gauss

Figure 2. EPR Spectrum of Organic Free Radical Peak and Vanadium(IV) Peaks.

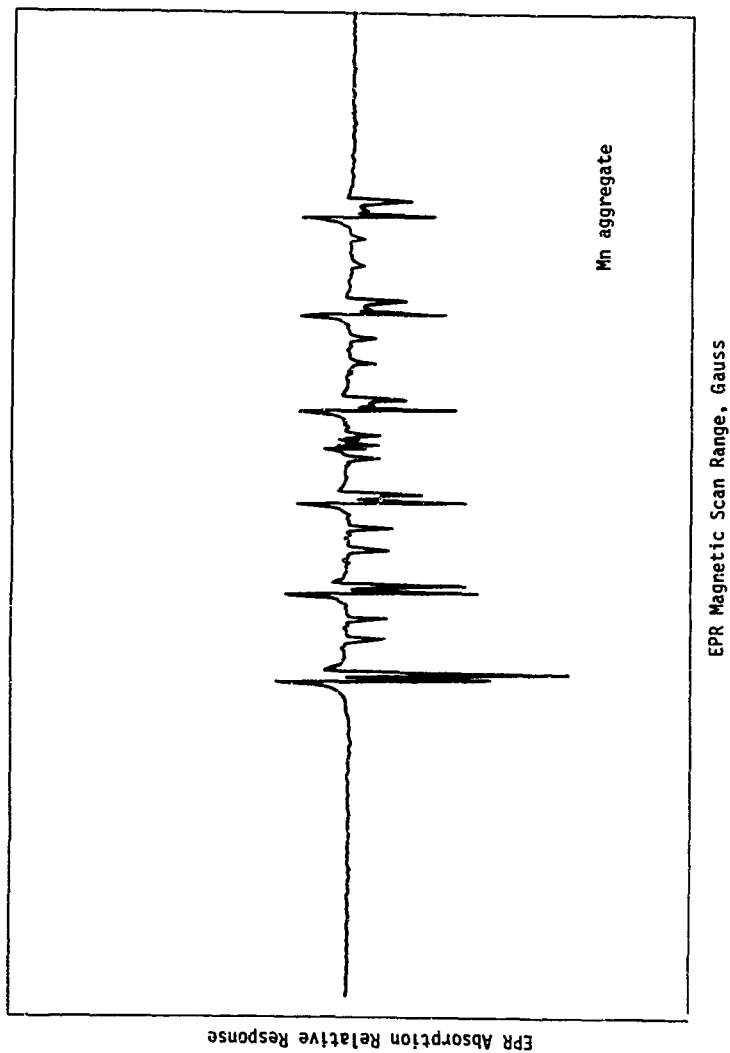


Figure 3. EPR Spectrum of Manganese(II).

where

x = unknown

[x] = concentration of unknown

std = standard

[std] = concentration of standard

scan = scan range (gauss)

gain = gain (obtained from instrument)

mod = modulation (obtained from instrument)

g = splitting factor

s = spin of electron

Area = area of curve

R = constant for each species (organic free radical and vanadium(IV))

The spin concentrations are expressed as spins per centimeter of the sample tube, or spins per gram of sample. Each species is calculated separately, so data is reported as spin concentration of the organic free radical and spin concentration of the vanadium(IV). To convert the spins per centimeter concentration measurement to spins per gram, 1 centimeter of the tube length is cut and weighed, and the weight of the tube material in the 1-centimeter length subtracted to find the weight in grams of its contents.

Results and discussion from the testing program are presented in the next section.

SECTION IV

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION FROM PHASE I

Phase I results showed several trends that formed the basis of the investigation for Phase II. Each of these trends is listed and discussed here, to provide background information for continuity into Phase II. In Phase I, EPR spectra were obtained for a variety of materials including neat asphalts, modifiers, blends, RTFO-conditioned materials, clay-gel fraction, recovered aged binders, and extracted binders from aged mixtures. Phase I (a scoping and screening phase) provided only qualitative data, in order to maximize the amount of quantitative information from select samples in Phase II. Although no spin concentration measurements were obtained on these materials in Phase I, the nature and significance of changes and/or differences between samples were evaluated by inspection of the obtained spectra. Listed below with a short discussion are the results and observations from Phase I.

The first observation was that a crude source gives a unique and obvious spectrum. Three asphalts from Chevron, and several others from other producers, were analyzed. All tested Chevron products showed spectra having similar organic free radical peaks with little or no vanadium(IV), while other asphalts from other producers showed varying amounts of vanadium and organic free radicals. Although concentrations were not calculated then, spectral inspection clearly showed that each set of asphalts from the same manufacturer was unique.

The second observation was that the AC (asphalt concrete) grading had little or no apparent effect on the spectra. As mentioned above, the same three Chevron asphalts, though of different viscosity grades, showed no obvious differences in the spectra observed.

Clay-gel fractions were obtained from a variety of materials which included neat asphalts, modifiers, blends, and extracted aged binders. The saturate and aromatic fractions of all the samples showed no organic free radical or vanadium(IV) peaks. However, the polar and asphaltene fractions

contained concentrations of organic free radicals and vanadium, if the original whole asphalt also contained vanadium. This observation led to further investigation of this correlation, which is discussed in the presentation of results from Phase II.

A solvent study was conducted to determine whether asphalt properties are affected by solvents, which are used in many other spectroscopic analysis techniques to dissolve asphalt specimens. Several asphalts were dissolved in a variety of solvents including methylene chloride, benzene, and trichloroethylene. For all solvents and asphalts tested, addition of a solvent to an asphalt specimen caused the organic free radical and vanadium(IV) peaks to disappear from the spectra. The solvent was then slowly evaporated, and the spectra taken at each stage of evaporation. During evaporation, the free radical and vanadium(IV) spectral peaks slowly reappeared, reaching original levels when evaporation was complete. This result, although not yet explained satisfactorily, did demonstrate that solvents change asphalt properties. Accordingly, EPR spectra were obtained only on neat samples, through the remainder of research.

Some of the materials were subjected to RTFO conditioning, and their EPR spectra obtained before and after this conditioning, to determine the changes in the organic free radical and/or vanadium(IV) concentrations. The results of this study indicated that RTFO conditioning caused minimal changes in the EPR spectra. Rather than prove that RTFO does not age the binder, however, this does show that RTFO conditioning is not severe enough, and does not take into account the aggregate interaction with aging to show significant changes in the EPR spectra.

The addition of modifiers to asphalts was also investigated. EPR spectra were separately obtained on an asphalt and a modifier, prior to mixing the two. After blending, a spectrum was taken. As expected, no significant change in the spectrum was observed because most modifiers (specifically, recycling agents) are highly aromatic or paraffinic oils, with few or no asphaltenes. As noted earlier, the saturate and aromatic fractions contain little or no unpaired-electron species.

Three aggregates were analyzed, using EPR. Two of the aggregates contained large amounts of iron, which has a broad EPR spectral peak with no fine structure. The third aggregate, however, contained manganese(II), which gives a six-line spectrum containing fine structure. This was noteworthy since manganese(II) is catalytically active, as is vanadium(IV), but has not been investigated further in Phase II, due to lack of available resources.

Atmospheric oxygen in the sample was studied to investigate reports that oxygen had altered the spectra of some samples. A number of samples were prepared, and spectra taken on each before and after evacuation, and after atmospheric oxygen was allowed to reenter the sample tube. From an analysis of results on all test samples (which showed no problems associated with the presence of atmospheric oxygen), it was determined that evacuation of EPR analysis samples was not necessary.

RESULTS AND DISCUSSION FROM PHASE II

Phase II chemical characterization (the major emphasis of Phase II testing) is subdivided in three subsections: (1) total vanadium concentrations, utilizing atomic absorption; (2) clay-gel separation percentages; and (3) results from the EPR analysis. Relationships between the physical and chemical results are also discussed. As mentioned earlier, several samples were used in the spin concentration measurement, and three asphalts (Huntway AC-40, Husky AC-5, and Chevron AC-20) were used for detailed aging studies.

Physical Characterization

Viscosity data obtained at 140°F for selected materials used in this study are listed in Table 2, which shows viscosities of unaged and aged (154 days) extracted binders. Three materials (Huntway AC-40, Husky AC-5, and Chevron AC-20) were chosen for detailed analysis. The initial viscosity measurements were taken on the neat material before mixing with the aggregate. The aging index for each material was calculated and is also listed in Table 2. This index is usually calculated after RTFO conditioning. For this study, however, the aging index was calculated after the 154-day aging process, causing the numerical values obtained to be significantly higher

than those reported by other researchers. The justification for this variance is that the EPR spin concentration measurements were taken first on the neat material, and again after the 154-day aging period. This modification of aging index was made to maintain consistency and make correlations.

Chemical Characterization

Table 3 lists the total vanadium concentrations obtained from the same select samples mentioned above, plus other samples that looked promising from the initial EPR spectral analyses. Also, included in this table is the total vanadium concentration for the polar compounds and asphaltenes of Huntway, Husky, and Chevron materials. The total vanadium concentrations were calculated from atomic absorption data, and are expressed as ppm in the total sample. The Huntway, Husky, and Chevron materials were also analyzed for total vanadium content after the 154-day aging process. Those values are listed in Table 3. It was observed that the vanadium concentration increased with aging. This may be because when mixed with the aggregate and aged, the binder incorporated some additional vanadium from the aggregate. This is only a hypothesis, however, because no analysis was performed on the aggregate.

Table 3 shows several interesting trends. First, the total vanadium concentrations for Chevron AC-10, Chevron AC-20, and Chevron 85/100 are very close to one another. This observation of identical vanadium(IV) concentration in materials of different viscosity from the same manufacturer (and possibly the same crude source) was reported in the Phase I interim report. A wide range of values was observed in the materials tested. The values ranged from 18 ppm of vanadium in the Diamond Shamrock material, to 1520 ppm in the Georgia AC-30 sample. The analysis also showed that most of the vanadium is found in the asphaltene fraction, with a small amount in the polar compounds. This particular observation is significant because other studies have shown that, when the asphaltenes are removed from the asphalt sample, the oxidation and formation of additional asphaltenes is reduced to almost zero. When the asphaltenes are placed back in the maltene phase, the asphaltene formation

TABLE 3. TOTAL VANADIUM CONCENTRATIONS.

Asphalt	V_t (unaged), ppm	V_t (aged), ppm
Huntway, neat	298	467
Huntway, asphaltenes	439	---
Huntway, polars	138	---
Husky, neat	254	311
Husky, asphaltenes	870	---
Husky, polars	189	---
Chevron AC-20, neat	48	112
Chevron AC-20, asphaltenes	306	---
Chevron AC-20, polars	36	---
Georgia AC-30	1520	---
Chevron AC-10	<30	---
Mississippi AC-20	33	---
Diamond Shamrock	18	---
Chevron 85/100	32	---
NavaJo 85/100	28	---

rate returns to normal*. This shows that the asphaltenes play a major role in the further oxidation, aging, and asphaltene formation. Figure 4 shows a plot of total vanadium concentration versus vanadium(IV), calculated in ppm. The information obtained from this analysis will be discussed later, in relation to the vanadium(IV) concentrations measured by the use of EPR.

Table 4 lists the clay-gel compositional analyses data for Huntway, Husky, and Chevron materials. The values shown in Table 4 include the fraction percentages for the neat asphalts, plus those for the binder extracted from the mixtures after 154-day aging. The changes in each fraction are calculated by subtracting the unaged percentage for each fraction from the aged percentage for that same fraction. In all cases, the asphaltene content increased, and the aromatics and polars decreased. This trend is expected because during the aging process, the oxidation products formed result in increased molecular polarity and more structuring. Perhaps, if the aromatic fraction can oxidize to form polar molecules, the polars will then oxidize further to form asphaltenes. It is impossible to quantify the percentage of aromatics that have been oxidized to polars and remain as polars, and how many original and new polars are being oxidized to asphaltenes. However, the asphaltene increase is quantifiable, and this fraction is thought to be the final result of oxidation and aging. The changes in these fractions will be discussed later in the subsection dealing with the EPR analysis.

Table 5 lists EPR spin concentration measurements for the materials in which quantitative analysis was performed. These concentration measurements include the organic free radical concentrations and the vanadium(IV) concentrations. In addition, the changes in these concentrations upon aging were calculated for Huntway, Husky, and Chevron materials, and are listed in Table 5. These changes are obtained by subtracting the unaged concentration from the aged concentration, so that correlations can be made with aging index and changes in the clay-gel fractions upon aging. Several parameters have

*Discussion with Chevron Research personnel.

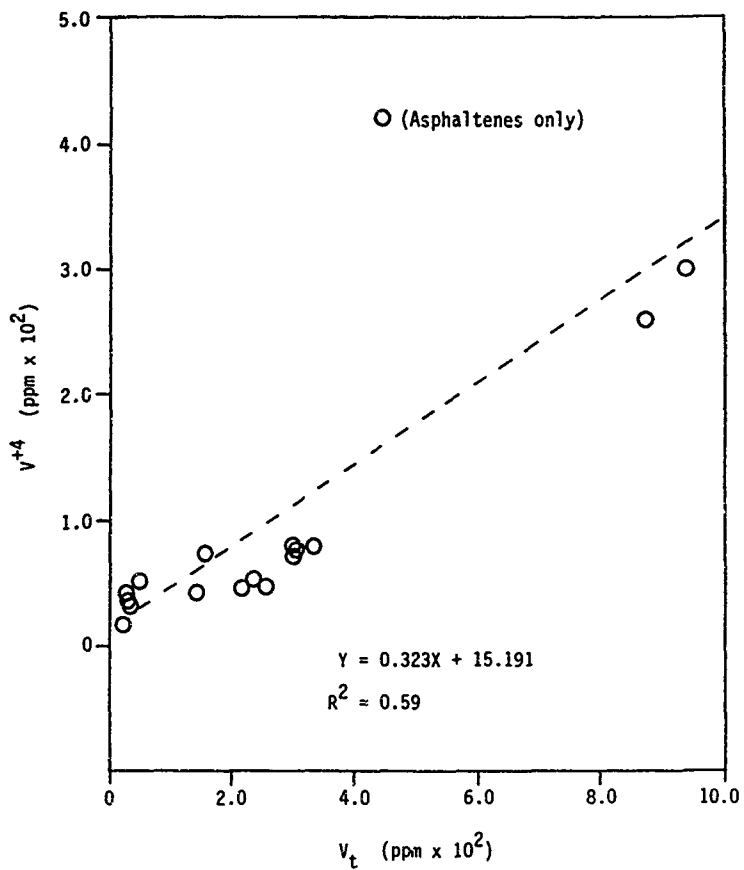


Figure 4. Vanadium(IV) versus Total Vanadium.

TABLE 4. CLAY-GEL COMPOSITIONAL ANALYSIS.

Asphalt	Asphaltenes, %	Saturates, %	Aromatics, %	Polars, %
Huntway, unaged	30.09	9.42	15.67	44.80
aged	43.43	8.24	11.78	36.55
change	13.34	-1.18	-3.89	-8.25
Husky, unaged	30.47	12.86	19.93	36.73
aged	33.96	12.19	18.90	34.94
change	3.49	-0.67	-1.03	-1.79
Chevron, unaged	19.80	19.88	16.52	43.81
aged	29.52	20.27	11.18	39.03
change	9.72	0.39	-5.34	-4.78

TABLE 5. VANADIUM AND FREE RADICAL SPIN CONCENTRATIONS.

Asphalt	V ⁴⁺ , spins/g	Organic free radical, spins/g
Huntway, unaged aged	1.01 x 10 ¹⁵ 6.47 x 10 ¹⁴	1.56 x 10 ¹⁵ 1.31 x 10 ¹⁵
Husky, unaged aged	5.80 x 10 ¹⁴ 6.64 x 10 ¹⁴	2.08 x 10 ¹⁵ 2.68 x 10 ¹⁵
Chevron, unaged aged	6.24 x 10 ¹⁴ 1.97 x 10 ¹⁴	3.24 x 10 ¹⁵ 2.11 x 10 ¹⁵
Huntway, asphaltenes polars	4.99 x 10 ¹⁵ 5.29 x 10 ¹⁴	1.09 x 10 ¹⁶ 3.82 x 10 ¹⁴
Husky, asphaltenes polars	3.11 x 10 ¹⁵ 7.52 x 10 ¹⁴	2.67 x 10 ¹⁵ 8.89 x 10 ¹⁴
Chevron, asphaltenes polars	9.47 x 10 ¹⁴ 5.18 x 10 ¹⁴	2.40 x 10 ¹⁶ 1.06 x 10 ¹⁵
Georgia, AC-30	3.20 x 10 ¹⁵	9.62 x 10 ¹⁴
Chevron, 85/100	4.13 x 10 ¹⁴	4.66 x 10 ¹⁵
Marathon, AC-20	6.36 x 10 ¹⁴	2.49 x 10 ¹⁵
Chevron, AC-10	5.09 x 10 ¹⁴	3.07 x 10 ¹⁵
Mississippi, AC-20	3.98 x 10 ¹⁴	6.24 x 10 ¹⁵
Navaajo, 85/100	2.22 x 10 ¹⁴	3.50 x 10 ¹⁵
Diamond Shamrock	2.85 x 10 ¹²	5.68 x 10 ¹³

been calculated using the data found in Table 5. First, however, the vanadium(IV) spin concentration values for several tested materials were converted to vanadium(IV) concentrations in units of ppm, to enable comparisons between the total vanadium values and vanadium(IV) concentrations. Figure 4 illustrates this correlation. Also using the concentrations in ppm values for both total vanadium and vanadium(IV), a ratio is calculated and expressed as V_t/V^{+4} . This ratio indicates the amount of total vanadium that is in the +4 oxidation state. The vanadium(IV) unaged concentration is subtracted from the aged concentration. This same calculation was performed on the organic free radical concentration values of the aged and unaged material. These last three parameters were obtained on Huntway, Husky, and Chevron because mixes of those materials were prepared and aged.

Figure 5 is a plot of V_t/V^{+4} versus aging index for the three materials used in the aging study. This plot illustrates that as the ratio of total vanadium to vanadium(IV) increases, the aging index increases. The correlation appears to be linear with the function

$$y = 14x + 12 \quad (3)$$

where y is the aging index and x is the V_t/V^{+4} ratio. The limited data indicates a relationship between total vanadium/vanadium(IV) concentration and aging index. The total vanadium and vanadium(IV) concentrations are obtained from the neat material before any aging has taken place; therefore, it is not necessary to age materials for long periods of time to obtain this ratio can be eliminated. Figure 6 also illustrates the relationship between aging index and the change (ΔR) in the free radical concentration between aged and unaged. The equation assuming a linear fit is

$$y = 34\Delta R + 68 \quad (4)$$

where y is again the aging index. An increase in free radical concentration appears to be indicative of a high aging index (large viscosity increase). This may result from the formation of free radicals during oxidation.

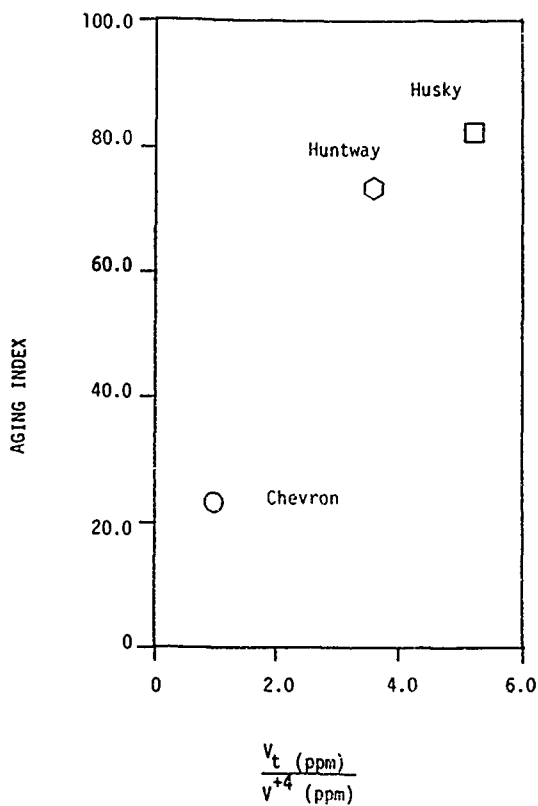


Figure 5. Aging Index versus V_t/V^{+4} .

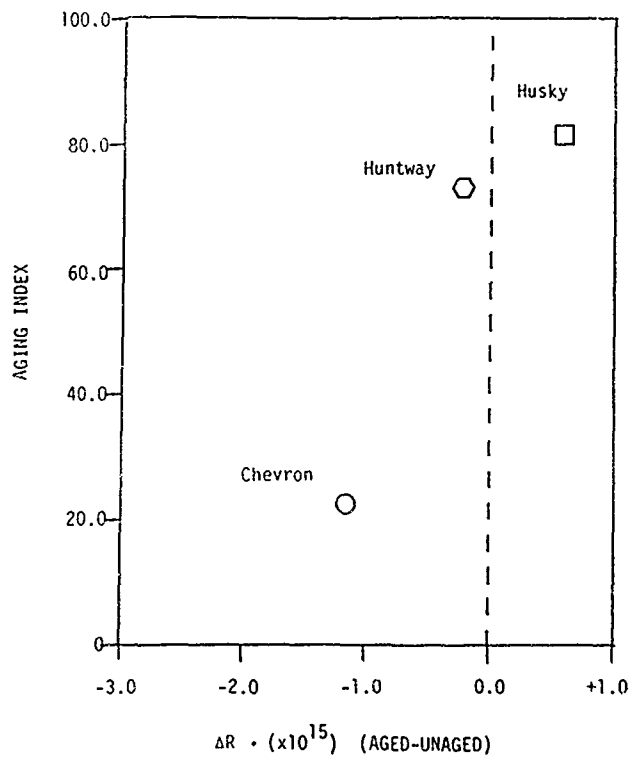


Figure 6. Aging Index versus ΔR .

In both of these figures, the trends are clear even though the number of materials investigated is limited. Figure 7 plots the change in vanadium(IV) concentration upon aging against aging index. This relationship is not linear, but indicates that there may be an upper limit in the change of V^{+4} beyond which the aging index no longer increases significantly.

Figure 8 describes the correlation between the change in aromatic percentage upon aging and V_t/V^{+4} . This is also a linear relationship defined by the equation

$$A = x - 6.7 \quad (5)$$

where A is the change in aromatic percentage. This is noteworthy because the aromatic content has been observed to change significantly upon aging in some asphalt materials; and in others, the change in aromatic content upon aging has been minimal (Reference 21). The kind of aromatic molecules found in this fraction, and the total amount of vanadium in the +4 oxidation state, may influence this change. In the materials tested in this effort, the change in aromatic percentage was apparently caused by the amount of the total vanadium in the +4 oxidation state.

Figure 9 plots the change in asphaltene content upon aging, against the V^{+4} concentration of the neat material.

Figure 10 depicts the change in aromatic percentages upon aging plotted against the change in the organic free radical concentration change upon aging. Again, based on a limited number of data points, the correlation appears to be linear with the function

$$A = 0.5\Delta R - 2.8 \quad (6)$$

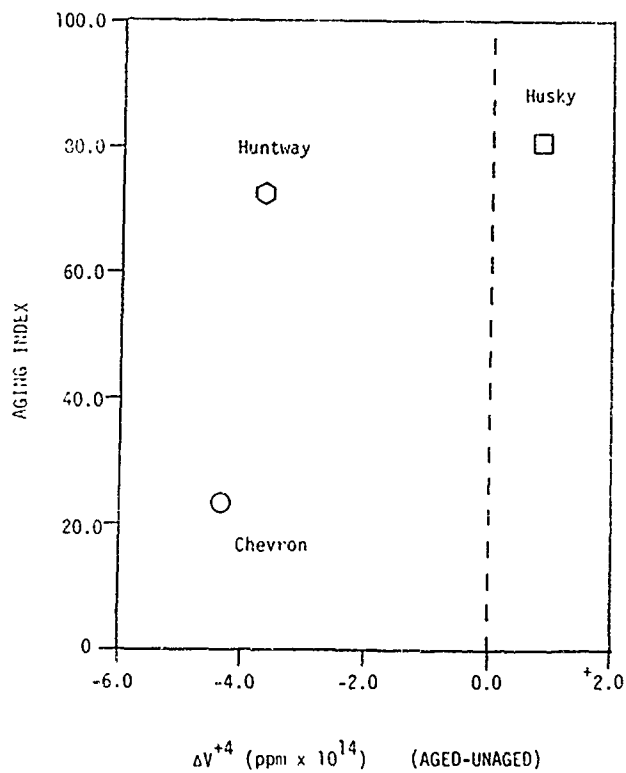


Figure 7. Aging Index versus ΔV^{+4} .

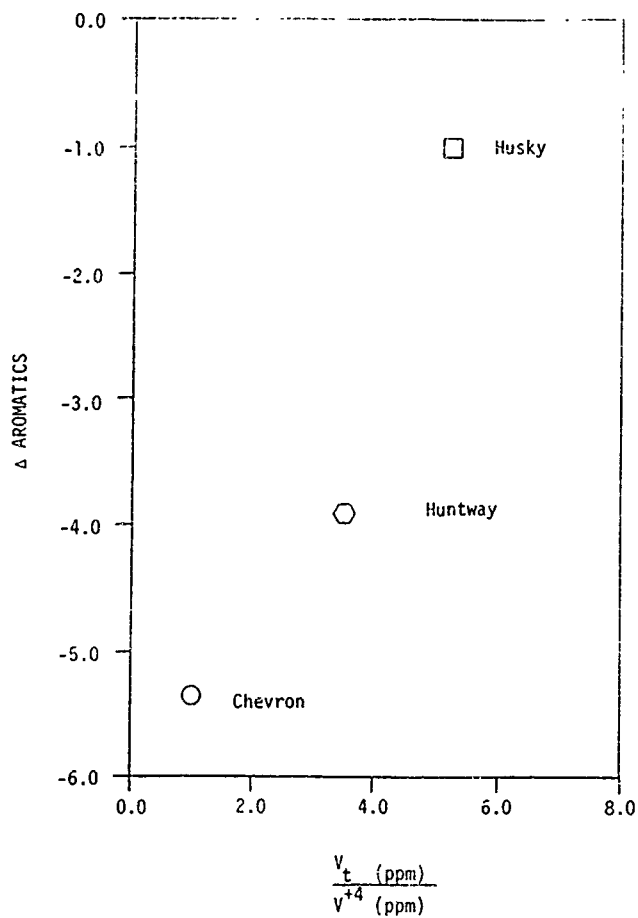


Figure 8. Change in Aromatics versus V_t/V^{+4} .

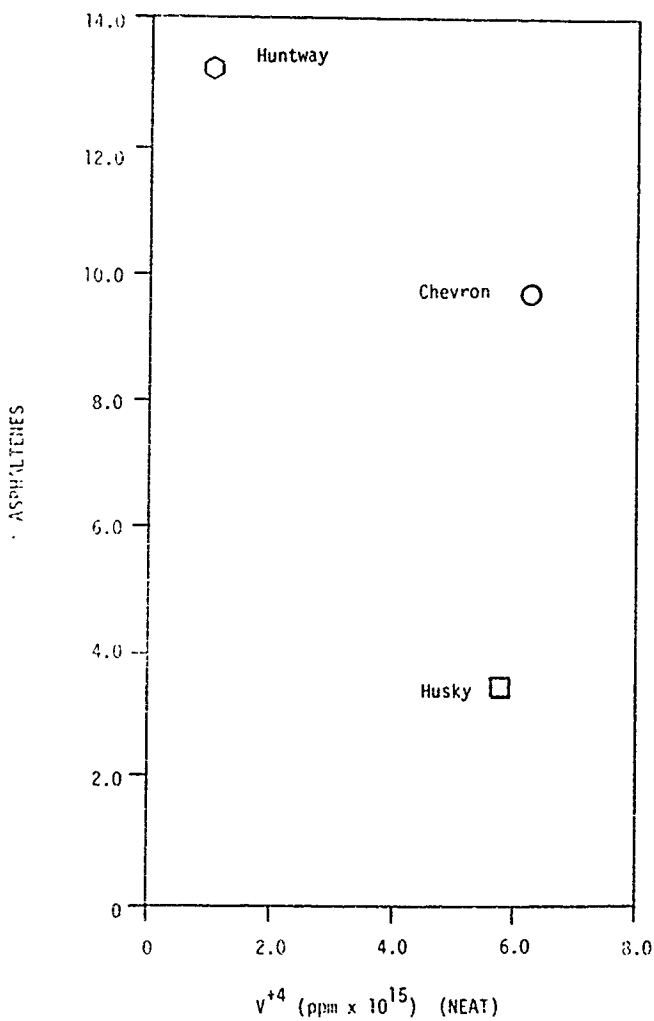


Figure 9. Change in Asphaltenes versus V^{+4} .

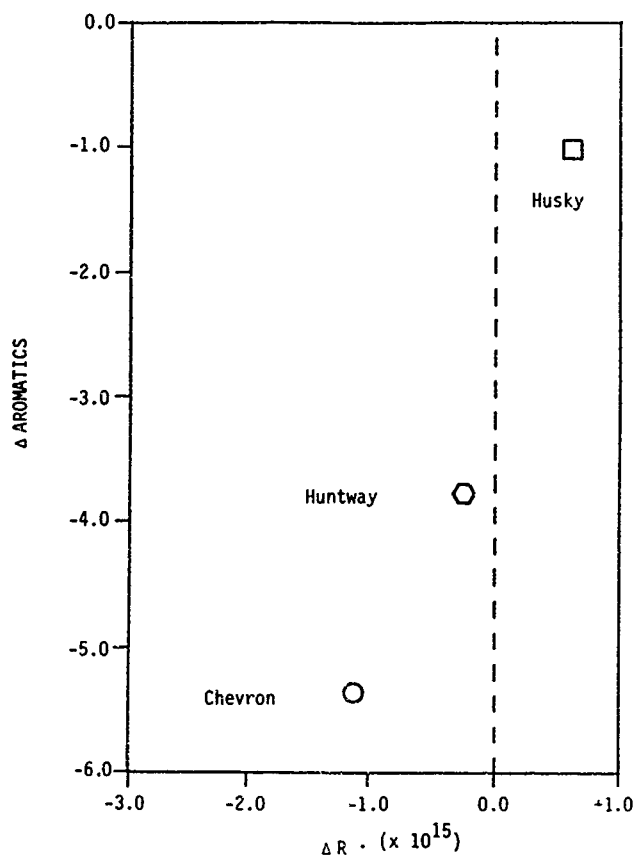


Figure 10. Change in Aromatics versus ΔR .

In summary, the experimental data show that the unpaired electron species play an important role in the oxidation and aging processes occurring in these materials. This is demonstrated specifically in Figures 5 and 6 in which the aging index is plotted versus parameters determined by EPR. Again, in Figures 8 and 10, a relationship between EPR parameters and clay-gel fraction changes has been established. The main advantage of using EPR to study asphalts is that asphalts can be analyzed in their neat state, without using solvents that destroy the interaction between molecules, consequently altering the properties of tested materials.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Several conclusions based on the data obtained from this effort are listed below:

1. Each set of asphalts from a particular producer shows a unique, characteristic spectrum. This was illustrated in the three samples from Chevron, and in representative spectra from a variety of other producers.
2. There is little relationship between asphalt viscosity and the total amount of vanadium or vanadium(IV) in the material. It might be thought that the greater the viscosity of an asphalt, the greater the concentration of vanadium, based on the fact that the higher viscosity material will contain more asphaltenes. However, this has not been the case. For instance, Georgia AC-30 has the greatest amount of total vanadium and the greatest amount of vanadium(IV), while Huntway AC-40 has a smaller amount of each.
3. Solvents do influence the material, as shown in the solvent studies. Whether or not they dilute the sample so that interactions between molecular species cannot be seen is not known at this time; however, they do play a part in changing the material.
4. The asphaltene and polar fractions contain most of the unpaired electron species such as organic free radicals and vanadium(IV). This continues to emphasize the importance of these two fractions in the oxidation process, as mentioned in the literature review (References 18 and 19), as well as the fact that asphalts do not oxidize at the same rate when the asphaltenes are removed from the material.

5. It appears that the aging index can be predicted from the V_t/V^{4+} ratio. This conclusion is important because the V_t/V^{4+} ratio can be obtained without any time-consuming aging process. The change in the organic free radical concentration upon aging can also be related to the aging index. These relationships illustrate that unpaired electron species play a significant role in the aging process.

6. The V_t/V^{4+} ratio, and change in organic free radical concentrations, can be related to changes in the aromatic fraction upon aging. The nature of the aromatic molecules may play an important role in the catalytic activity of the vanadium(IV) and the organic free radicals, which are extremely reactive.

7. This study shows that vanadium(IV) and the organic free radicals are involved in the aging process, and that some vanadium catalytic activity is indicated.

RECOMMENDATIONS

Based on the results, analyses, and conclusions from this initial effort, work in the area of EPR analyses of asphaltic materials should be continued. While a limited number of materials were studied, trends which indicate the direction of further studies have become clear. Significant questions have arisen. The following recommendations are made for additional research in this area.

1. More asphalts need to be included in the analyses, especially with regard to the aging process and, hence, development of an equation relating the V_t/V^{4+} to the aging index. Then, an approximate aging index could be calculated by obtaining the total vanadium content and the vanadium(IV) concentration, and the time-consuming, artificial aging process would be eliminated.

2. Aggregate influences should be investigated further, to determine the influences of catalytically active species found in the minerals.

3. Temperature studies should be investigated. By running EPR under low temperature, the iron spectrum can be obtained and analyzed for influences on the aging and oxidation processes. The influence of high temperatures on bitumens should also be examined. It is known that high temperatures can cause the format' free radicals.

4. The influence of ultraviolet radiation needs to be studied. Ultraviolet radiation can also cause formation of free radicals and degradation of pavement surfaces. It must be resolved, whether or not this radiation causes the formation of enough radicals to influence the oxidation process.

REFERENCES

1. Nellenstyn, F. J., Journal of Institutional Petroleum Technologists, Vol 10, p. 311, 1924.
2. Shirey, W. B., "Metallic Constituents of Petroleum," Industrial Engineering Chemistry, Vol 23, p. 1151, 1931.
3. Dunning, H. N., Bieber, H., Williams, R. B., Moore, J. W., "Porphyrin, Nickel, Vanadium, and Nitrogen in Petroleum," Journal of Chemical Engineering Data, Vol 5, p. 546, 1960.
4. Saraceno, A. J., Fanale, D. T., Coggenshall, N.D., "An Electron Paramagnetic Resonance Investigation of Vanadium in Petroleum Oils," Analytical Chemistry, Vol 33, p. 500, 1961.
5. Roberts, E.M., Rutledge, R. L., Wehner, A. P., "Determination of Vanadium and Free Radical Concentrations in Crude Petroleum by Electron Magnetic resonances," Analytical Chemistry, Vol 33, p. 1879, 1969.
6. Retcofsky, H. L., Thompson, G. P., Hough, M., Friedel, R. A., "Organic Chemistry of Coal," American Chemical Society, Chapter 10, pp. 142-155, 1978.
7. Retcofsky, H. L., Hough, M. R., Maguire, M. M., Clarkson, R. B., "Coal Structure," American Chemical Society, Chapter 4, pp. 37-58, 1981.
8. Boucher, L. J., Tynan, E. C., Yen, T. F., Electron Spin Resonance of Metal Complexes, Plenum Press, New York, pp. 111-132, 1964.
9. Boucher, L. J., Tynan, E. C., Yen, T. F., "Spectral Properties of Oxovanadium (IV) Complexes," Inorganic Chemistry, Vol 7, No. 4, April 1968.
10. Yen, T. F., Erdman, J. G., Saraceno, A. J., "Investigation of the Nature of Free Radicals in Petroleum Asphaltenes and Related Substances by Electron Spin Resonance," Analytical Chemistry, Vol 34, No. 6, May 1962.
11. Tynan, E. C., Yen, T. C., "Association of Vanadium Chelates in Petroleum Asphaltenes as Studied by ESR," Fuel (London), 43, 191, 1961.
12. Dickson, F. E., Kunesch, C. J., McGinnis, E. L., Petrakis, L., "Use of Electron Spin Resonance to Characterize the Vanadium (IV) - Sulfur Species in Petroleum," Analytical Chemistry, Vol. 44, No. 6, May 1972.
13. Shibata, K., Kakiyama, H., Sanada, Y., Sohma, J., "E.S.R. Study of Vanadyl Complexes in Various Carbonaceous Materials at High Temperatures," Fuel, Vol. 58, No. 12, December 1979.
14. Seehra, M. S., Srinivasan, G., "Electron Spin Resonance from Impurities in Coal-Derived Pyrites," Fuel, Vol. 61, No. 4, April 1982.

REFERENCES (CONCLUDED)

15. Duber, S., Wieckowski, A. B., Jones, P. M., Lee, M., "E.P.R. Study of Molecular Phases in Coal," Fuel, Vol. 62, No. 3, March 1983.
16. Das, U., Doetschman, D. C., Jones, P. M., Lee, M., "Electron-Spin Echoes and Saturation in Coal," Fuel, Vol. 62, No. 3, March 1983.
17. Sebor, G., Kubelka, V., Weissner, O., "Separation and Characterization of Vanadylporphyrins from Romashkino Petroleum," Czechoslovakia Chemical Communication, Vol. 44, 1979.
18. Branthaver, J. F., Nazir, M., Peterson, J. C., Dorrance, S. M., "The Effect of Metalloporphyrins on Asphalt Oxidation: I. Effect of Synthetic Metal Chelates," Liquid Fuels Technology, Vol. 1 (4), pp. 355-369, 1983.
19. Branthaver, J. F., Nazir, M., Peterson, J. C., Dorrance, S. M., Ryan, M. J., "The Effect of Metalloporphyrins on Asphalt Oxidation: II. The Effect of Vanadyl Chelates Found in Petroleum," Liquid Fuels Technology, Vol. 2 (1), pp. 67-89, 1984.
20. Pepera, M. A., Callahan, J. L., Desmond, M. J., Milberger, E. C., Blum, P. R., Bremer, N. J., "Fundamental Study of the Oxidation of Butane over Vanadyl Pyrophosphate," Journal of the American Chemical Society, Vol. 107, pp. 4883-4892, 1984.
21. Kiggundu, B. M., Nusser-Humphrey, B. J., and Zallen, D. M., Recycling Agent Selection and Tentative Specification, ESL-TR-84-47, Final Report to AFESC, March 1985.

APPENDIX A

MODIFICATIONS TO CLAY-GEL COMPOSITIONAL ANALYSIS,
FORMERLY ASTM D-2007-75

The clay-gel compositional analysis method formerly designated ASTM D-2007-75, was modified by the New Mexico Engineering Institute (NMERI) to meet the requirements of Subtask 5.01. In the original ASTM round-robin tests, polars did not exceed 25 percent, and saturates were greater than 20 percent. NMERI modified the original D-2007 method to improve mass balance, and to accommodate analysis of a variety of asphaltic materials with varying percentages of asphaltenes, polars, saturates, and aromatics. These modifications are described in this appendix.

Two of the modifications made to the ASTM method were performed prior to its use by NMERI. The first modification was to strip the column of aromatics, rather than calculate the aromatic fraction by difference as stipulated in the ASTM method. This change was made because the original method causes error if recovery of polars from the clay column is incomplete. When this occurs, erroneous lumping of the recovered polars into the aromatic fraction causes the results to show incorrectly low polar content, and an incorrectly high aromatic fraction.

The second modification affected the calculation of polar percentage. The ASTM D-2007-75 method for calculating this percentage for a polar sample of 5 grams or less, is shown in equation A-1 below.

$$\text{percent polars} = 0.88 \times \frac{\text{grams of polars recorded}}{\text{grams of total sample}} \times 100 \quad (\text{A-1})$$

The factor 0.88 in equation A-1 was established experimentally, to maintain continuity of results over a wide range of polar compounds. To provide a true mass balance, this factor was eliminated from the calculations.

The following additional modifications, incorporated to correct test problems, improved the repeatability of results.

AMOUNT OF SOLVENT TO PRECIPITATE ASPHALTENES

The maximum pentane usage for asphaltene precipitation was increased. This maximum (after all washing) was originally set at 250 to 300 milliliters (ml), of which 100 mL was designated for asphaltene precipitation from the asphalt sample. After using 300 mL of pentane during tests, however, the filtrate coming through the funnel was still very dark in color, showing that the maltene fraction was still being held onto the asphaltene fraction. (Asphaltene molecules are highly polar, and are capable of hydrogen bonding to the polar molecules of the maltene fraction.) To separate total maltenes, the amount of pentane was increased. A pentane maximum usage of 1500 mL was found sufficient to recover the maltene fraction for a variety of asphalts with varying amounts of polars and asphaltenes. If the filtrate becomes clear before 1500 mL is used, the maltenes are completely separated from the asphaltenes, and pentane addition can be discontinued. The amount of pentane needed for precipitation is directly proportional to the percentage of asphaltenes in the sample.

SAMPLE SIZE

Sample size was reduced for samples containing high polar percentages. As stated in the ASTM procedure, when the polar content of a sample exceeds 20 percent, a sample size reduction is warranted because the polar absorption capacity of the clay column is limited. In the ASTM procedure, a 5-gram sample is the upper limit for highly polar samples. However, a 2.5-gram sample size is used in the modified procedure. This smaller size ensures that the clay column is not being overloaded and has produced excellent repeatability in all materials tested.

SOLVENT SYSTEM FOR POLARS

For reasons of safety and utility, the original ASTM method was modified. The ASTM method stipulated a maximum of 300 mL of a 50/50 mixture of benzene to acetone by volume to strip the polar column. In the modified NMERI method, benzene has been replaced by toluene because benzene is a carcinogen.

Also changed were the solvent mixture ratio and maximum amount. Because the clay column eluent was still dark in color after 300 mL of solvent addition, the solvent mixture was altered to 30-percent toluene and 70-percent acetone, and solvent maximum usage was increased to 1500 mL, or until the eluent was clear.

The use of acetone raised concern by several researchers consulted, because acetone adds ketone functionality to the fraction which manifests itself as additional carbonyl absorbances when using infrared spectroscopy as a second technique. In response, methanol was tried as a replacement for acetone in the solvent. Methanol use was rejected, however, because toluene/acetone has a solubility parameter closer to that of benzene/acetone, and was believed to give a better separation.

SOLVENT SYSTEMS FOR AROMATICS

A solvent system was developed to strip the aromatic column and achieve mass balance. In the modified procedure used by NMERI, a solvent system of 70-percent toluene/30-percent methanol was used to strip the silica-gel column and recover the aromatic fraction. Care is needed to ensure that the methanol is dry, and that no more than 30 percent of methanol is used, because the silica gel reacts with the water and/or methanol, causing heating of the column. This can result in column fracture at the fitted joint, if the column is not constructed properly.

ADDITIONAL FINAL ELUENT

To ensure that all material is being efficiently stripped from the columns, a final modification was made to the solvent systems for the polars and aromatics. Using the modified procedure, the aromatic column is charged with 100 mL of pure toluene as a final eluent. The polar column is charged with 200 mL of methylene chloride as a final eluent.

ELIMINATION OF CALCIUM CHLORIDE

The last NMERI modification to the ASTM D-2007 clay-gel technique was to delete the use of calcium chloride and a separatory funnel for removing water from the polar compound eluent. This step was discarded because it was cumbersome and time consuming. In the modified procedure, molecular sieves were employed to dry the solvents before use.

USE OF ROTARY EVAPORATOR

Solvent evaporation was enhanced by a rotary evaporator, raising the efficiency and thoroughness of this process and reducing the time required.